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Part 1

Fifth Edition

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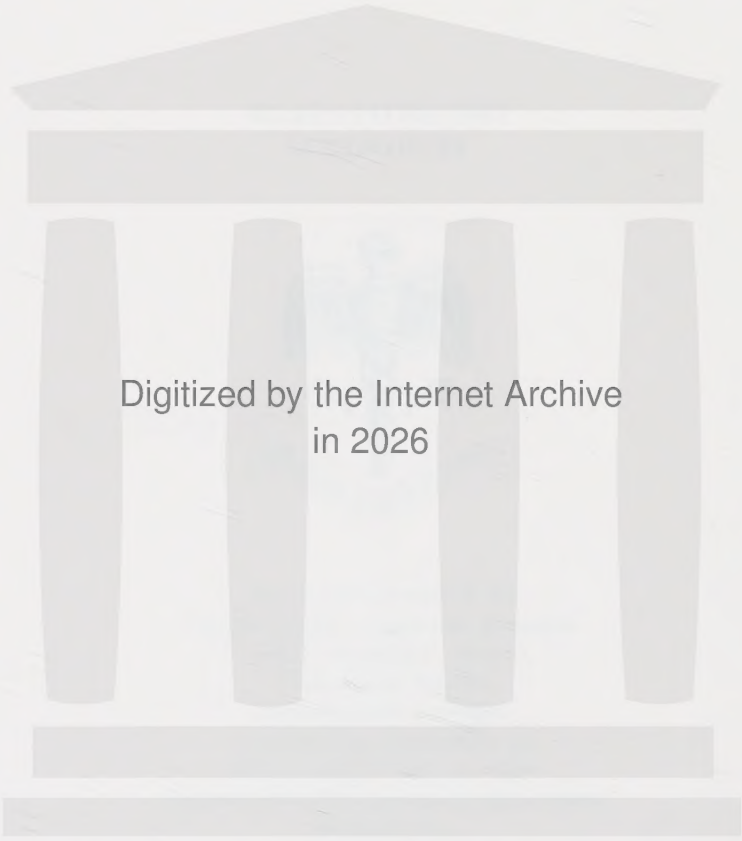
MODERN PETROLEUM TECHNOLOGY

THE INSTITUTE OF PETROLEUM

The Institute acquired its crest,
designed by the College of Heralds, in 1949
Its motto, 'Conjunctione Potiores'
(strength through unity),
supports a shield portraying
the Archaeopteryx, an avian fossil
which was found in Jurassic strata
similar in age to important oil-bearing formations
in the North Sea



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MODERN PETROLEUM TECHNOLOGY

5th Edition
Part I

Edited by

G. D. Hobson
B.Sc., Ph.D., D.I.C., F.G.S., A.R.S.M., S.P.E.,
A.A.P.G., F.Inst.Pet.

on behalf of
The Institute of Petroleum, London

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Chichester . New York . Brisbane . Toronto . Singapore

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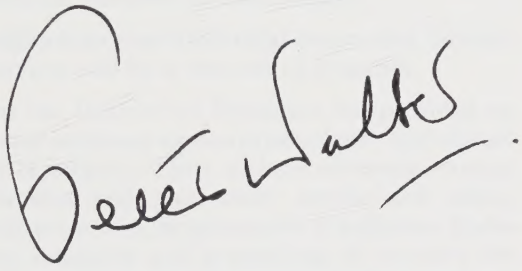
FOREWORD

I am pleased to have been asked to write a foreword to this new edition of 'Modern Petroleum Technology'. It is eleven years since the previous edition of this authoritative oil handbook, produced by the Institute of Petroleum, was first published. In that period, fundamental changes have occurred in the energy field and to the vital role in it of oil and gas. When the last edition appeared, the huge increases in the price of oil had only just begun to affect the world economy, and the need for change and for greater emphasis on efficient energy conservation was only just being recognized. Eleven years ago, the United Kingdom's own North Sea oil development was only just coming into fruition. Today, Britain is among the top six largest oil producers in the world.

At this time of rapid change in the oil industry, 'Modern Petroleum Technology' provides, in two volumes, an excellent handbook for specialists and non-specialists alike. It provides a quick reference to most aspects of the technology of the oil industry and I warmly commend it.



PETER WALKER
(Secretary of State for Energy)
London, 1984

THE INSTITUTE OF PETROLEUM

The Institute of Petroleum, a scientific society, originally known as the Institution of Petroleum Technologists, was formed in 1913.

The objectives of the Institute are:

To give objective consideration to the science, technology and economics of petroleum and its products and their uses, to express an informed viewpoint on such matters as well as to provide a forum for discussion and the exchange of ideas.

To disseminate expertise between its own committees, between the Institute and other organizations and with appropriate government departments.

To promote a flow of information of a factual nature about the science, technology and economics of petroleum and, in this connection, about the work of the Institute and the petroleum industry.

To provide appropriate services to members, both individual and collective, including opportunities for individual members to meet socially.

These objectives are met through a structure of technical committees, through publications and information services and by a network of branches.

THE IP'S ROLE: For 70 years the Institute of Petroleum has provided an impartial forum for the discussion of technical aspects of petroleum. Specialized committees cover a wide range of subjects. These include education, energy economics, engineering, exploration and production, health and safety, measurement, research, standardization, and the prevention of pollution. Codes of practice, measurement tables, standards and proceedings of symposia are produced and published. *Petroleum Review,* the Institute's informative and readable magazine, is despatched to members each month. In addition to the excellent Library, the Institute has an Information Department. Conferences and Seminars are also arranged.

MEMBERSHIP: The three categories of membership are: Student Member (S.Inst.Pet), from the age of 18 to 25*; Member (M.Inst.Pet), who should be not less than 21 years of age; and Fellow (F.Inst.Pet.). A Fellow must have been a Member for not less than 5 years, must satisfy Council that he has appropriate professional, technical, scientific or academic qualifications and have held a position of responsibility concerned with petroleum for not less than five years. An organization, such as a company, may become a collective member and may nominate a representative who is entitled to all the privileges of an individual member, except that he may not serve on Council or use an abbreviated membership designation.

BRANCHES: In addition to the thirteen branches of the IP in the United Kingdom, there are three overseas branches in Ireland, Kuwait and Singapore.

THE INSTITUTE'S TECHNICAL WORK: There are ten main technical committees, some of which have sub-committees, panels and working groups.

* Proposals to raise this upper age limit are in hand.

They have a total membership of over 1000 experts in the various fields, primarily from the oil industry, but also from government departments and other bodies. They are supported by the qualified members of the technical department of the Institute.

THE INSTITUTE'S INFORMATION ACTIVITIES: Standard technical works used internationally by the petroleum industry and allied bodies, as well as reports on IP conferences and symposia, are published each year.

Technical papers, data sheets and booklets on oil industry subjects are produced regularly.

The IP's magazine, *Petroleum Review*, has a wider circulation than the IP membership and is an informative and topical oil industry journal, dealing in depth with subjects of wide interest.

The Library and Information Departments deal with an increasing number of enquiries from members and the general public, by telephone, by mail and in person. These are well in excess of 11,000 a year. In 1981, the Library, which has 15,000 volumes, added on-line information searching to its facilities, which links the IP to 150 important data bases, mainly in North America.

The conferences organized each year by the IP include a wide range of technical and economics subjects, and range from half-day to residential conferences. The branches have their own lectures and social programmes.

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LIST OF CONTRIBUTORS

ARROWSMITH, A.
Lecturer in Chemical Engineering, University of Birmingham

ASHTON, N.
Lecturer in Chemical Engineering, University of Birmingham

BANKS, R. E.
Reader in Chemistry, University of Manchester Institute of Science and Technology

BARBER, S. W.
Control Engineer, B.P. Shipping Ltd.

BARNETT, T. G.
L.P.G. Technical Supervisor, B.P. Oil Ltd., London

BELL, L. H.
Senior Scientist, Esso Research Centre, Esso Petroleum Co. Ltd.

BERRIDGE, S. A.
Berridge International Consultants, Nottingham

BEZER, H. J.
Senior Development Physicist, Burmah Castrol Ltd.

BODDY, J. H.
Formerly Mobil Europe Inc.

BRAMLEY, J.
Technical Support Manager, Shell Chemical International Trading Company

CHIPPERFIELD, E. H.
Senior Bitumen Consultant, British Petroleum Oil International Ltd.

DUCKWORTH, P. S.
Research Superintendent, Burmah–Castrol Ltd.

FALCON, N. L.
Formerly Chief Geologist, B.P. Trading Ltd.

HADLEY, D, J., O.B.E.
Formerly Research Adviser, B.P. Chemicals International Ltd.

HANCOCK, E. G.
Formerly Shell International Chemical Co. Ltd.

HARPER, F. D.
Technical Manager Bitumen, Esso Petroleum Co. Ltd.

HOBSON, G. D.
V. C. Illing & Partners, Cheam, Surrey (Emeritus Reader in Oil Technology, Imperial College of Science and Technology, London)

JENNER, J. W.
Drilling Manager, B.P. Petroleum Development (Overseas) Ltd.

JONES, P.
Assistant General Secretary (Technical), Institute of Petroleum, London

JONES, W. M. C.
Formerly Pipelines Inspector, Department of Trade and Industry, London

JOWETT, F.
Technical Director, Astor Chemical Company, West Drayton

KING, G. A. B., C.B.E.
Formerly Managing Director, B.P. Shipping Ltd.

KING, P. J.
Senior Lecturer in Chemical Engineering, University of Manchester Institute of Science and Technology

KNIGHT, H.
Laboratory Superintendent, Burmah–Castrol Ltd.

MATTHEWS, G. B.
Visiting Professor in Exploration Geophysics, University College, London

MAY, C. J.
V. C. Illing & Partners, Cheam, Surrey

MCDERMOTT, C.
Lecturer in Chemical Engineering, University of Birmingham

MCPHERSON, L. J.
Business Technical Support Department, B.P. International Ltd.

MILLER, J. E.
Senior Instrument Engineer, Shell U.K. Oil

MILLS, A. L.
Technical Director, Burmah–Castrol and Veedol International

MILSOM, J.
Lecturer in Exploration Geophysics, University College, London

Olive, M. F.
Business Technical Support Department, B.P. International Ltd.

Owen, K.
Automotive Fuels Department, Esso Research Centre, Esso Petroleum Co. Ltd.

Paddock, K. F.
Head of Pipelines Inspectorate, Department of Energy, London

Plummer, D. P.
Formerly Shell (U.K.) Ltd., Shell Centre, London

Priestley, R.
Lecturer in Chemical Engineering, University of Birmingham

Reynolds, B.
Technical Support Manager, Honeywell Control Systems Ltd., Ascot

Selwood, P.
Technical Secretary, U.K. Offshore Operators Association, London

Shipman, R. H.
Manager, Environmental Services, B.P. Oil Ltd., London

Spicer, F. E. H.
Group Head, B.P. Research Centre, British Petroleum Co. p.l.c.

Turner, L.
Section Head—Laboratory, Shell Amsterdam Shell Test Method Standardisation Centre

Turner, L.
Formerly B.P. Chemicals International Ltd.

Thomas, R. F.
Formerly Senior Design Engineer, B.P. Shipping Ltd.

Veale, B. L.
Head of Fleet Design and Development, B.P. Oil Ltd.

Vere, R. A.
Formerly Principal Scientist, Aviation Fuels Research, Esso Research Centre, Esso Petroleum Co. Ltd.

Williams, A. E.
Laboratory Superintendent, Burmah–Castrol Ltd.

Wills, R. J. A.
Senior Development Chemist, Burmah–Castrol Ltd.

I

The Occurrence and Origin of Oil and Gas

By G. D. HOBSON

PETROLEUM, etymologically, means rock oil or mineral oil, but in modern technical usage it has a wider meaning which includes natural gas, mineral wax and bitumen, in addition to crude oil. In some contexts oil and petroleum can be used interchangeably, yet there are others in which clarity or custom requires oil rather than petroleum, or vice versa. Thus, to most people oil industry and petroleum industry are synonymous, yet, for good reasons, it is the practice to speak of oilfields or gasfields, but rarely of petroleum fields.

What is an oilfield? This question can be answered with certainty in considerable detail. Natural curiosity also poses the question, 'How are oilfields formed?' So far this query has not been answered completely, although the problem has become more clearly defined, and now there is much information on the formation of petroleum. The mode of origin of oilfields is not merely a matter of academic interest, for the greater the advance towards the full solution of this complex problem the more intelligently and effectively can the search for new oilfields be carried out.

THE NATURE OF OIL AND GAS ACCUMULATIONS

At an early date it was recognized that hydrocarbon accumulations required the existence of a reservoir rock to store the fluids and something, normally a cap rock, to prevent their escape. In addition to these readily appreciated requirements, the idea developed that there must be a source rock in which the oil and gas were formed. The rocks acting as the reservoir and cap are obvious for any accumulation; the source rock of a given oil and gas accumulation may be a matter of debate.

Reservoir Rock

A reservoir rock must possess fluid-holding capacity and fluid-transmitting capacity. The former property is referred to as porosity and the latter as permeability. A variety of different types of openings in rocks are responsible for these properties in reservoir rocks. The commonest are the pores between the grains of which the rocks are made. However, in some rocks there are cavities inside fossils, openings formed by solution or by volumetrically incomplete replacement, and fractures or joints which have been created in various ways. The relative importance of the different kinds of openings varies with the rock type, but pores usually account for the bulk of the storage space. The effective porosity from the point of view of oil storage is that afforded by the continuously connected openings, and such openings alone provide the property of

permeability. Although a rock must be porous in order to be permeable there is no simple quantitative relationship between porosity and permeability. Furthermore, reservoir rocks show far greater variations in permeability than in porosity. In addition, the values of these properties, as measured on cores of reservoir rocks obtained in drilling wells, are not always identical with the values indicated for the rock in bulk underground. The differences arise from the non-representative nature of cores when there are wide variations in the sizes of the openings in the rocks, and also from irregularities in their distribution. Porosities are generally in the range 5 to 30 per cent, whilst permeabilities are commonly between 0.005 darcy and several darcys, as measured on small samples.

Pores are usually only a very small fraction of an inch in width, whereas fossil and solution cavities may sometimes approach or exceed an inch in width. Many joints and fractures are probably only a small fraction of an inch across, although they may extend for considerable distances.

Most reservoir rocks are sedimentary rocks, and almost always the coarser grained of the sedimentary rocks, namely, sands, sandstones, grits, limestones, and dolomites. Rarely do shales act as reservoir rocks, but when this is the case they contain 'fractures', for their pores alone are much too small to give adequate permeability. Similarly there are occasional cases of igneous and metamorphic rocks serving as reservoir rocks, and again fractures and other relatively wide openings are believed to have conferred the required reservoir properties on an otherwise unpromising rock.

Cap Rock

The cap rock acts as a seal to prevent the escape of oil and gas from the reservoir rock. Typical cap rocks are clays and shales, rocks in which the pores are very much finer than those of reservoir rocks. Other rocks, such as marls and dense limestones, for example, also can serve as cap rocks, provided that any pores are very small, and that the rock is free from joints and cracks. There are cases where so-called evaporites (salt, anhydrite, gypsum) act as cap rocks. A rock with plastic rather than brittle properties, when in place in the earth's crust, is most effective as a cap rock.

A cap rock has a far lower permeability than a reservoir rock, although it will be realized that low permeability cannot be the truly effective property. It is more direct to note that cap rocks have very high capillary pressures, and reservoir rocks have much lower capillary pressures (see Table VII). The capillary pressure is the pressure required to cause a fluid to displace from the openings in a rock another fluid with which it is not miscible; capillary pressure is dependent on the size of the openings, the interfacial tension between the two fluids, and the contact angle for the system.

Fluid Distribution in the Reservoir Rock

The distribution of the fluids in a reservoir rock is dependent on the densities of the fluids and the detailed capillary properties of the rock. Taking the simplest case of a rock in which the pores are of uniform size and evenly distributed, there will be an upper zone where the pores are filled mainly by gas (the gas

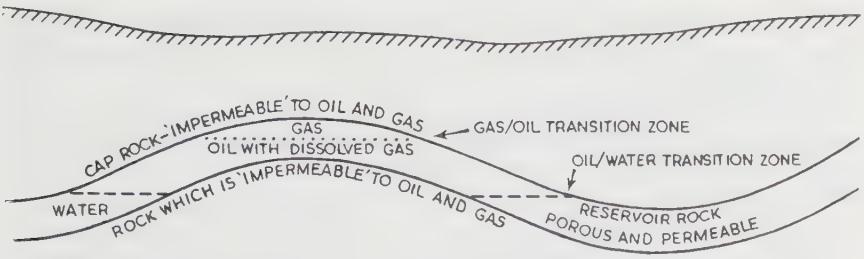

FIG. 1. Vertical cross-section of an anticlinal accumulation of oil and gas. Showing cap and reservoir rock, and the main features of the arrangement of the fluids in the reservoir rock. The section could be of the order of 2 miles or more in length.

cap), a middle zone in which the pores are occupied principally by oil with gas in solution, and a lower zone with its pores filled by water (Fig. 1). A certain amount of water occurs along with the oil in the middle zone, the proportion often being of the order of 10 to 30 per cent. There is a transition zone from the pores occupied entirely by water to pores occupied mainly by oil in going upwards in the reservoir rock. The thickness of this transition zone depends on the densities and interfacial tension of the oil and water, and on the sizes of the pores. Similarly there is some water in the pores in the upper gas zone which has at its base a transition zone from pores occupied largely by gas to pores filled mainly by oil in going downwards. The water found in the oil and gas zones is known generally as interstitial water. This interstitial water occurs as collars around grain contacts, as a filling of pores with unusually small throats connecting with adjacent pores and to a much smaller extent as wetting films on the surface of the mineral grains when the rock is preferentially wet by water (Fig. 2).

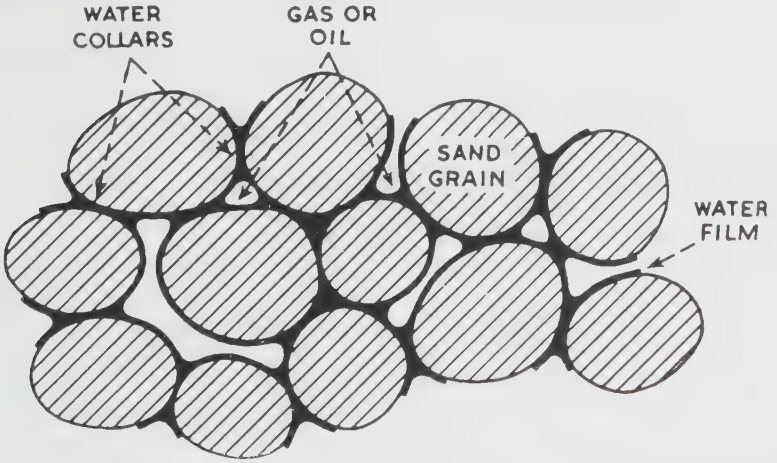

FIG. 2. Much enlarged section of a small part of a reservoir rock containing gas or oil, to illustrate the detailed distribution of water and hydrocarbons. Water is shown as wetting films (relative thickness greatly exaggerated), as collars around the grain contacts, and in some completely filled pores. The three-dimensional network of pores allows continuity to exist for the hydrocarbons via connections which would be in front of and behind the section shown.

The so-called gas–oil and oil–water contacts are generally horizontal. However, in certain circumstances these fluid contacts are inclined, usually only very gently.

It will be evident that a cap rock is a rock that is not penetrated by oil or gas. Sometimes for part of an accumulation the oil or gas has its lower boundary marked not by the water-bearing zone of the reservoir rock, but by adjacent sealing rock which must possess the same characteristics as the cap rock.

There are hydrocarbon accumulations consisting of gas only, in which cases there will be a gas–water transition zone. On the other hand, when the pressure and temperature conditions are suitable in relation to the proportions and the nature of the gas and oil, there will be no gas cap, but only oil with dissolved gas overlying the water.

Traps

Oil and gas cannot be retained as an accumulation unless there is a trap, and this requires that the boundary between the cap rock, or other sealing agent, and the reservoir rock shall be, in principle, convex upwards. The exact form varies very widely. In terms of this description the simplest forms are the flat-lying convex lens, and the anticline and dome, each of which has an upper surface roughly resembling an inverted saucer or boat. Many oil and gas accumulations are trapped in anticlines or domes, structures which are generally more easily detected than some types of trap.

Some traps are formed by the reservoir rock being cut off at its upper end by a fault which places sealing rock against the fractured end (Fig. 3). Alternatively, the upper end may have been eroded away during a period of unconformity, with the subsequent covering of the eroded top of the reservoir rock by a sealing rock (Fig. 3). These are, respectively, a fault and one of the wedge-out types of trap.

There are cases where the reservoir rock wedges out at its upper end as an

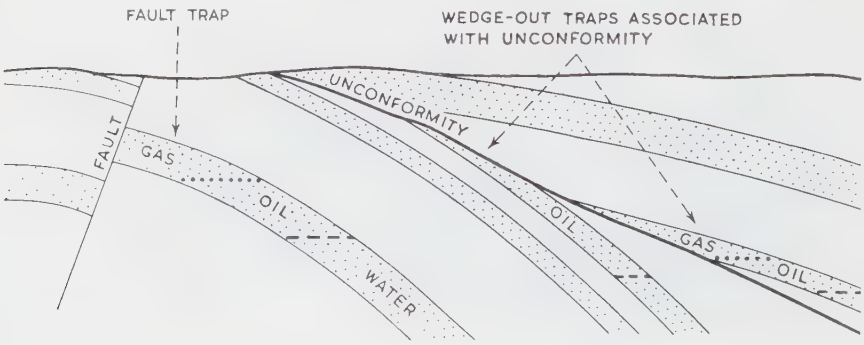

FIG. 3. Vertical cross-section to show several types of trap. All could occur in close proximity as shown; on the other hand they could occur singly in widely separated areas. The inclination of the beds could be greater or much less than drawn. The reservoir-rock type of sediment is marked by stippling; the cap-rock type has been left blank. Surface geological mapping might, in favourable circumstances, have indicated the presence of a fault and an unconformity.

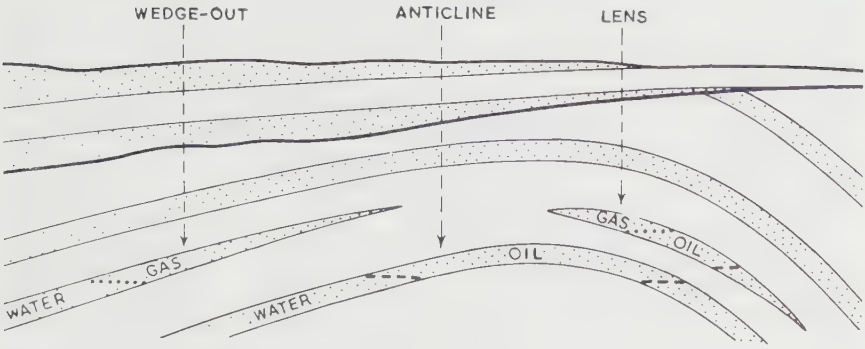

FIG. 4. Vertical cross-section showing several kinds of trap. Note that the form of the near-surface strata gives no indication of the existence or of the nature of the traps.

original depositional feature due to lateral variation in deposition (Fig. 4) or abuts against an old land surface (Fig. 3). These also are wedge-outs or stratigraphic traps.

Traps associated with salt intrusions are of various kinds (Fig. 5), while limestone reefs (Fig. 6) can serve as reservoir rocks and can also give rise to overlying traps of anticlinal form as a result of differential compaction.

Finally, examples occur in which the reservoir rock extends to the surface of the earth, but oil and gas are sealed in it by clogging of the pores by bitumen or by natural cements.

Although it has been convenient to describe these various types of trap as separate entities, it should be noted that many reservoirs have more than one of the factors listed contributing to the trapping of the hydrocarbons.

The Fluids

The gas in many fields is mainly methane. Small amounts of the next higher members of the paraffin series occur in it, especially when oil is present, and the proportions of these and other light hydrocarbons in the vapour phase rise considerably when the hydrocarbon accumulation is under high pressure and at a relatively high temperature. In the case of gas-condensate accumulations the liquid oil recovered at the surface is entirely in the vapour phase in the reservoir rock, and is roughly comparable in make-up with the gasoline fraction of more usual crude oil. Commonly there are appreciable amounts of non-hydrocarbon gases, and occasionally such gases are the dominant components. Nitrogen, carbon dioxide, and hydrogen sulphide are the main non-hydrocarbon gases. Some gases have traces of helium, and a small number have concentrations of helium of commercial importance.

Crude oils range widely in their physical and chemical properties. Green, brown and black are common colours, and there are rare examples of almost white or straw-coloured oils. The specific gravities are mainly between 0.73 and 1.02, most crudes having specific gravities lying between 0.80 and 0.95. These values are for surface conditions of temperature and pressure. Data for a considerable number of crude oils indicate kinematic viscosities of 0.007 stokes to 13 stokes at 100 °F, the bulk of the values being in the range 0.023 to 0.23

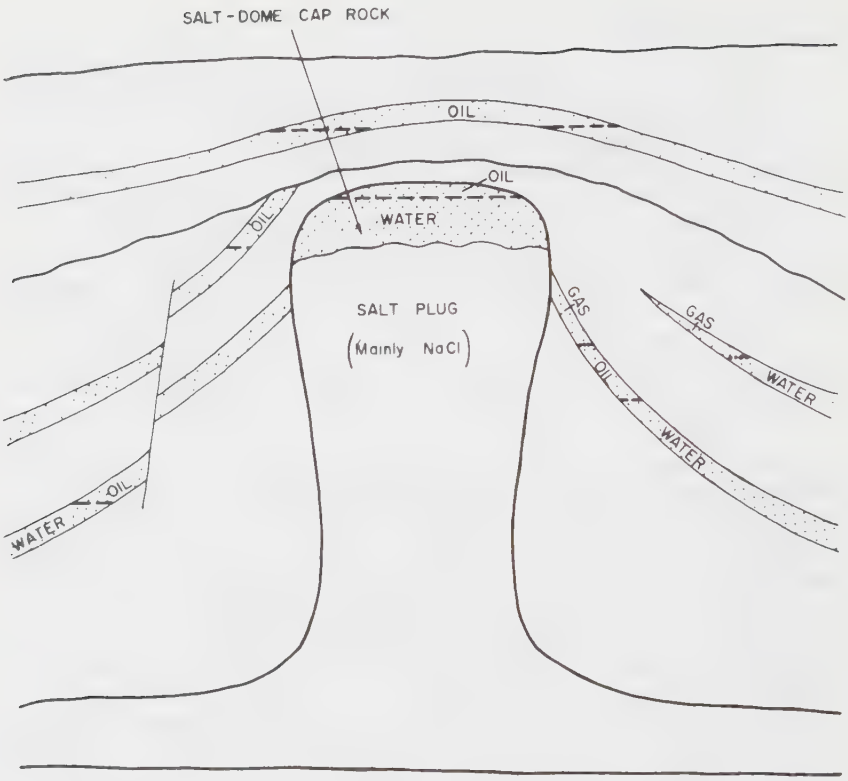

FIG. 5. Much simplified cross-section showing a salt dome. A number of different types of traps can be associated with salt intrusions. This feature, together with the structural complexities around and at times over the intrusion, can render exhaustive testing for oil and gas accumulations both difficult and costly. Not all salt domes have oil and gas accumulations.

stokes. Under subsurfaces conditions, with higher temperatures and gas in solution, densities and viscosities are lower than for surface conditions.

In terms of elements, crude oils are composed principally of carbon and hydrogen; sulphur, oxygen and nitrogen, when present, are usually small in amount. The carbon/hydrogen ratio is usually between 6 and 8. A wide range of metallic elements have been found, generally as traces, in the small amount of ash obtained by burning many crude oils.

The main types of hydrocarbons present in crude oils are paraffins, naphthenes, aromatics, and hybrids involving combinations of these types. They range widely in boiling point, and many cannot be distilled under atmospheric pressure without breakdown. Naphthenic acids, complex nitrogen compounds, and mercaptans account for some of the oxygen, nitrogen, and sulphur present in crude oils. In addition, the resinous and asphaltic substances present in some crudes contain oxygen and sulphur.

Chlorophyll porphyrins have been found in small amounts in many crude oils. These compounds indicate a contribution from plant sources, a comparatively low-temperature history, and probably a reducing environment.

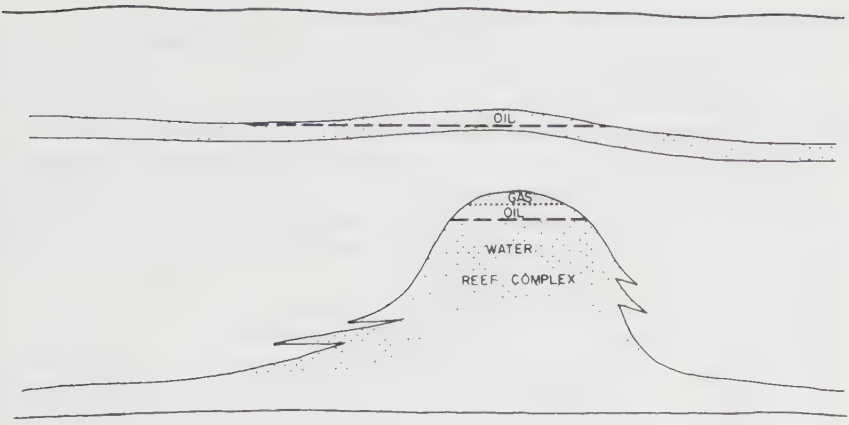

FIG. 6. Simplified section of limestone reef. The reef may contain oil and gas. Its reservoir properties can be variable. Arching of overlying strata can give traps as a result of differential compaction of the rocks surrounding and overlying the reef. Such traps are comparable with those developed by differential compaction over buried hills created by erosion.

Animal-type porphyrins have been detected in smaller amounts, but it is now known that comparable porphyrins, in some respects, may be derived from plant sources. Isoprenoid hydrocarbons have been recognized; these compounds have structures typical of substances formed biologically. Other hydrocarbon structures with biological affinities have been detected.

The proportions of the main types of hydrocarbons vary from one crude oil to another, and these proportions have been used as a basis for the broad classification of crude oils into paraffin-base, mixed-base, and asphalt-base. Many members of each type are present, and crude oils are complex by reason of the number and variety of the compounds they contain. Nevertheless, the lighter fractions at least are less complex than was formerly thought to be the case. Thus, in nearly forty years' work the Ponca City crude oil had yielded 234 compounds (all but four being hydrocarbons), with boiling points from $-161.48\,^{\circ}C$ to $475\,^{\circ}C$, and aggregating some 45 per cent by volume of the crude oil. A fuller account of the nature of crude oils is given in Chapter 9.

The water associated with oil and gas accumulations is usually markedly saline, and appears in many instances to be modified sea water, the principal differences being a deficiency in sulphates, relatively less magnesium, and commonly a greater concentration than normal sea water. Traces of hydrocarbons and organic acids are present.

Depths, Sizes, and Other Features

Hydrocarbons have been produced virtually from the grass roots down to more than 20 000 ft, and the deepest well yet drilled in search of oil reached 31 441 ft in Washita County, Oklahoma. The Drake well, drilled in 1859, found oil at a depth of 69 ft. The deepest oil production was from 21 465 ft at Lake Washington, South Louisiana; gas-condensate has been obtained from 21 190 ft

in Vermilion Parish, South Louisiana; while the deepest gas production is from the Ellenburger at 26 518 ft in Wheeler County, Texas Panhandle.

Oil has been produced from rocks of all ages from Pre-Cambrian to Pleistocene: the oil is not necessarily of the same age as the reservoir rock. The age of the producing formations varies from one area to another.

The temperature and pressure can be high in deep reservoirs. Temperature gradients in the earth's crust generally range 15°C/km to 50°C/km, while the fluid pressure is commonly equivalent to a gradient of about 0.43 psi/ft of depth, but sometimes it is less than this figure, and in other cases it approaches 1 psi/ft.

Oil reservoir rocks may be only a few feet thick; they may be hundreds of feet in thickness. The height of the hydrocarbon zone in a reservoir may range from a few tens of feet to several thousand feet. A structure may have one or a number of superimposed reservoir rocks, and in some cases there is comparatively thinly interbedded reservoir and non-reservoir rock over a vertical section more than a thousand feet thick, with the reservoirs so close together that groups of reservoirs are handled as one unit in a single well. On the other hand, when the individual reservoirs are more widely separated and sufficiently thick, production can be taken from them separately, although it may still be feasible to produce from two, three or even four reservoirs separately and simultaneously in a single well.

There is a convention under which each independent accumulation is described as a pool, whereas an oilfield consists of one or more pools associated with a given structure or limited area.

Reservoir rocks range from a few acres in extent to a hundred or more square miles carrying oil. Well spacing depends on the nature of the reservoir or reservoirs, with the result that wells located in accordance with currently accepted good practice may be only a few hundred feet or as much as a mile apart. Nevertheless, in some countries, for example Canada, well spacing is artificially determined by conservation regulations, and the wells may not then be placed at the points which would give the most efficient drainage of the reservoir. Initial producing rates from wells vary from less than a hundred to thousands of barrels of oil per day (a barrel is approximately 5.61 ft^3 and contains 35 UK gallons). Finally, ultimate recoveries from individual wells are similarly variable, generally ranging from tens of thousands to several million barrels of oil.

Many gas wells initially have producing rates of the order of several million or more cubic feet per day. Oil wells invariably produce gas along with the oil, the proportions ranging from less than 100 to more than 10 000 ft^3 of gas per barrel of oil. The proportions vary from one pool to another, and may change with the state of depletion of the pool. The ratio of total gas (free and dissolved gas) to oil varies widely with the oil and gas accumulation. Even if there were moderate constancy in the proportions formed (there is no evidence that this need be the case) there are various possible means which could lead to the proportions found in accumulations being different from the proportions formed.

The minimum size of an oil accumulation of commercial interest depends on many factors, including the depth, location, reservoir characteristics, and the properties of the oil. Many fields are relatively small, but considerable numbers initially had reserves of over 100 000 000 brl; some greatly exceed

1 000 000 000 brl. Ghawar in Saudi Arabia is estimated to have reserves of 75×10^9 brl. These figures refer to the oil expected to be obtained under stated economic and technical conditions; the actual oil present originally in each case would usually be several times greater than the recoverable reserves.

Gas accumulations are equally variable in size. Urengoy in Siberia is reported to have reserves of 176.5×10^{12} cu ft, while Leman Bank in the southern North Sea has been stated to have 12×10^{12} cu ft. At the lower end of the range Lockton in Yorkshire has been said to have produced 13×10^9 cu ft.

Table I shows the leading countries from the point of view of remaining oil reserves indicated at the end of 1981, together with their outputs during 1981

TABLE I
Oil Production and Reserves

	Millions of barrels of oil				
	Cumulative production to 31/12/81	Remaining reserves at 31/12/81*	1981 production	First production†	Peak producing year to date
Saudi Arabia	44 143	158 500	3 513	1936	1980
USSR	71 898	85 000	4 446	1863	1981
Kuwait	20 566	67 680	343	1946	1972
Mexico	8 743	48 084	844	1901	1981
Iran	30 111	39 432	504	1913	1974
Abu Dhabi	6 500	35 500	414	1962	1977
Iraq	15 924	33 700	365	1927	1979
USA	131 278	29 830	3 140	1859	1970
Libya	13 828	25 859	429	1961	1970
Venezuela	36 819	20 150	769	1917	1970
China	6 706‡	18 500	738	1939	1979
Nigeria	8 918	10 951	516	1957	1979
Indonesia	9 915	9 976	586	1893	1977
Norway	959	8 978	175	1973	1980
UK	2 494	7 643	650	1919	1981
Algeria	6 760	6 942	352	1914	1979
Neutral Zone	3 496	6 313	134	1954	1974
Canada	10 515	5 460	469	1862	1973
Egypt	2 349	3 530	229	1911	1981
Qatar	3 302	3 438	150	1949	1973

Based on information on World Oil issues and API's *Petroleum Facts and Figures*.

* These figures must be taken only as a guide. In some cases new discoveries are not included. They also differ in the quality of the basic data.

† In some areas small amounts were obtained before the date given.

‡ Includes estimated figures.

and their cumulative outputs at the end of that year. It seems likely that the natural gas resources (alone, as a gas cap, or in solution) are, in terms of calorific content, of the same order of magnitude as the crude oil resources.

Table II provides some information on natural gas reserves.

World oil production in 1981 was $20\,578 \times 10^6$ brl. Cumulative world production at the end of 1981 was estimated to be about $455\,832 \times 10^6$ brl, the remaining reserves at that date being placed at $660\,142 \times 10^6$ brl. L. G. Weeks has studied the many oil-bearing areas, and has estimated the ultimate primary

oil reserves to be 2×10^{12} brl, with a further 1.5×10^{12} brl to be expected from the application of secondary recovery techniques. Primary oil reserves are those recoverable by using the natural energy stored in and around the oil accumulations. In secondary recovery the natural energy is supplemented in various ways, such as by water injection, gas injection, subsurface combustion, or the injection of fluids miscible with the oil whereby interfacial phenomena which interfere with oil displacement are eliminated.

TABLE II

	Remaining natural gas reserves at the end of 1981 (estimated from different sources)*		Gas production in 1981
	10^9 cu ft	10^9 cu ft	10^9 cu ft
USSR	1 377 000	1 160 000	16 422
Iran	370 000	484 000	254
USA	199 100	198 000	19 581
Algeria	123 550	130 900	466
Saudi Arabia	113 393	114 000	358
Canada	91 000	89 900	2 609
Abu Dhabi	85 000	19 500	371
Mexico	75 352	75 350	1 089
Qatar	60 000	60 000	162
Norway	59 445	49 370	955
Netherlands	55 036	55 700	2 854
Nigeria	48 320	40 500	39
Venezuela	48 210	47 000	588
Malaysia	35 900	19 000	37
Libya	35 808	23 200	140
Kuwait	33 000	30 500	209
Indonesia	30 500	27 400	694
Australia	29 394	18 700	374
Iraq	25 250	27 300	23
China	25 300	24 000	672
World	3 203 222	2 911 346	55 001

* The volumes are given for low-pressure conditions (at or close to NTP). 6 000 cu ft of natural gas has a calorific value approximately equal to that of one barrel of crude oil.

A study of 74 oilfields and 38 gasfields in USA showed them to have had economic producing lives ranging from 14 to 87 years; the average life for the oilfields was 46 years and for gasfields 39 years. The half-life (time to produce half of the reserves) averaged 16 years for both types of fields; only 11 per cent of the fields had half-lives of 10 years or less, while 15 per cent had half-lives exceeding 20 years. The average time from discovery to the peak annual output was 11 years for the oilfields and 12 years for the gas fields; 13 per cent of the fields reached their peak annual output in under five years. The fraction of the reserves recovered in the first 10 years averaged 29 per cent for the oilfields and 30 per cent for the gas fields. The Bradford field, lying across the border between Pennsylvania and New York State, was discovered in 1871, had its first producing rate peak in 1881 and has had subsequent producing peaks as a result of the application of secondary (enhanced) recovery techniques.

THE FORMATION OF OIL ACCUMULATIONS

The problem of the mode of origin of oil accumulations has attracted attention for many years, yet to date it has not been completely solved. Some of the difficulties undoubtedly stem from the mobility of oil and gas, and from the fact that oil and gas accumulations will respond to disturbances of equilibrium and undergo changes in volume and position.

Views on the origin of oil and gas accumulations must take note of many facts. These include the following:

(a) The universal association of the accumulations with sedimentary rocks (even when in igneous or metamorphic rocks they are never far from sedimentary rocks).
(b) Their presence most commonly in marine deposits.
(c) Their occurrence in rocks ranging widely in age.
(d) Their presence in the locally high parts of the reservoir rocks.
(e) Although the temperatures and pressures are high in the deeper accumulations, there is no indication that all accumulations have attained these values, and the temperatures in particular are not high in comparison with those used in various laboratory and industrial operations concerned with the preparation of oil products.
(f) The absence or almost complete absence of olefin-type hydrocarbons in crude oils.
(g) Crude oils are not equilibrium mixtures.

Although the hydrocarbons occupy what is locally the highest available part of the reservoir rock, provided that there is no marked water flow, it is difficult to accept that this and no other part of the reservoir rock would be preferred for oil and gas formation, even if these substances were formed in that rock.

The Origin of Petroleum

The earlier hypotheses on the origin of petroleum postulated its generation from inorganic materials such as water acting on metallic carbides, or water and carbon dioxide interacting with alkali or alkaline earth metals. Alternatively, because of the detection of hydrocarbon material in some meteorites and in the atmospheres of certain planets, suggestions were made that hydrocarbons present in the primaeval earth gave rise to oil accumulations. These ideas find few if any supporters now, and the same is true of the hypothesis that petroleum is one of the products of vulcanism; they require some improbable materials or associations, or could be expected, if correct, to lead to a general pattern of oil and gas occurrence differing from that observed.

Quite early it was suggested that petroleum was formed from organic matter by transformation as a result of heating. This concept comes from the fact that destructive distillation of vegetable matter, coal and oil shale, carried out industrially, produced some oily products. These processes required quite high temperatures, and the nature of the products was affected by the temperature applied and by other conditions. Maier and Zimmerly carried out experiments on oil shale, of long duration at lower temperatures, and found that small

amounts of solvent-extractable material were formed at temperatures substantially below those employed industrially, and that the amount formed was a function of the temperature and the duration of heating—to a first approximation the time effect was linear and the temperature effect exponential. Thus, a given amount of extractable product could be formed in a shorter time at a high temperature than at a lower temperature.

An alternative and later suggestion by Cunningham-Craig, subsequently elaborated by Zobell, was that bacteria carried out the transformation of organic matter into petroleum. Certainly bacterial action on organic matter in sediments forms methane. Much later Whitmore and Meinschein proposed that petroleum was the product of collecting hydrocarbons and closely allied substances that had been formed in organisms.

Investigations, especially during the past twenty-five years, aided by major developments and increased sensitivity in analytical techniques, have provided a coherent story on the origin of petroleum which embraces the three agencies noted above, although thermally-induced changes appear to be of the main importance.

Crude petroleum is not an equilibrium mixture, and on a geological time scale its composition is slowly changing. S. R. Silverman found that heating at 121 °C for two weeks caused detectable changes, the low-molecular-weight components formed being isotopically lighter so far as the carbon was concerned, than the original.

Organisms differ in chemical composition, and their principal parts also differ in chemical make-up. The chief types of compounds are carbohydrates, proteins, lignins, and lipids, the last type including fats, fatty acids, and hydrocarbons. Immediately on the death of an organism chemical changes set in, and the process of decay varies in nature, rate and extent, depending on the environment and the part of the organism. A major determinant is whether the conditions are aerobic or anaerobic, that is whether free oxygen is present or absent. Broadly the presence of free oxygen leads to the more extensive early breakdown of the organic matter.

In order to contribute to the formation of petroleum the organic matter must be incorporated in sediments. This requires that the organic matter must grow in the area of deposition or be transported from its place of growth in particulate or soluble form, or adsorbed on inorganic mineral matter, and be deposited with inorganic mineral particles. Because of the low density of organic matter it will normally sediment only where water is still, an environment in which very fine-grained mineral matter, especially clay, is deposited. An exception to this could occur where the organism develops in or on inorganic matter in an aqueous environment and may therefore enter a sediment attached to that inorganic matter. Still water is depleted in dissolved oxygen, a feature of stagnant or anaerobic conditions, and so in it there is the prospect of the preservation of a greater proportion of the sedimented organic matter. Coarse mineral grains can be deposited in moving water, water which will have dissolved oxygen, and hence any organic matter that is also deposited will certainly initially be in an aerobic environment, and so liable to extensive early modification or destruction. It is possible, however, for sediments to be aerobic at the sediment/water interface, yet to become anaerobic after slight burial.

The organic carbon contents of many samples of recent and ancient

sediments have been measured. Excepting oil reservoir rocks the organic carbon content is very low in coarse sediments such as sands, but is appreciable in fine-grained sediments such as clay and shales (Table III).

Plant organisms are far more abundant than animal, and the latter are directly or indirectly when carnivorous, dependent on the former. Also animals excrete unconsumed organic matter, and in aqueous environments such excrement will add organic matter to the sediments, mainly vegetable residues. Plants may shed components as a normal activity while life continues. Some parts of plants survive in visually recognizable form with relatively little alteration in ancient sediments. There are also substances recognizable chemically as having originated from plants or animals, although some compounds may not be such specific indicators of an animal source as was once

TABLE III

Distribution of Organic Carbon Contents for Nearly 1400 Shale Samples

Organic carbon content (%)	Percentage of sample	Organic carbon content (%)	Percentage of samples
0.015–0.03	0.6	1–2	27.6
0.03–0.06	1.7	2–4	14.3
0.06–0.12	3.4	4 8	5.3
0.12–0.25	6.4	8–16	2.6
0.25–0.50	14.4	16–32	1.2
0.50 ·1.00	22.5		

thought to be the case. Overall it seems that the plant kingdom contributes most to the organic content of rocks. Moreover, the development of source rocks calls for the conditions to favour the growth of vegetable organisms comparatively nearby. Certain mineral nutrients are needed, in addition to sunlight. Near-shore areas and zones of upwelling of nutrient-bearing currents provide appropriate conditions for the vegetable organisms to grow in abundance.

Early changes in the sediment, in which micro-organisms play a part, cause much of the organic matter to be converted into an insoluble geopolymer—kerogen—which is an organic complex that is variable in type, in detailed composition, and in the nature of the potential products on breakdown. It seems that kerogen may account for 88 to 90 per cent of the organic matter in the sediments. Progressive burial, with which is associated a slow rise in temperature, leads to alteration of the kerogen and the formation or release of hydrocarbons and closely allied substances. Rates of burial and temperature gradients in sedimentary rocks vary widely (values as low as 5 °C/km and as high as 90 °C/km have been reported), and thus the attainment of a given temperature may require very different lengths of time. As noted earlier, the rates of change appear to be a linear function of time and an exponential function of the temperature level; it is the integrated time temperature factor which determines the overall changes in the kerogen, and hence the amount and detailed nature of the products.

Analyses of the solvent extracts from source rocks in a vertical sequence show certain trends as the depth increases. The ratio of saturated hydrocarbons or of aromatic hydrocarbons and the organic carbon content of the rock increases, although at different rates during the principal stage of oil formation, and the n- and iso-alkanes tend to increase relative to the other types of hydrocarbon. The distributions of the different types of hydrocarbon also change, so that the peak values occur at progressively lower carbon numbers. Among the cyclo-alkanes the proportion with a small number of rings increases.

The initial distribution of the odd- and even-carbon number n-alkanes is not identical in all source rocks: in some cases there is marked dominance of the odd-carbon-number compounds among the larger molecules. However, the generation of further hydrocarbons leads to suppression of this dominance.

These various changes are associated with the maturing of the source rock. Fig. 7 shows how the rate of generation of oil changes on burial, and also that later there are other changes that lead to increasing amounts of gas associated with the development of an immobile residue which progressively approaches graphite in composition.

In parallel with these changes in the solvent extracts there are changes in the appearance of spores and in the reflectance of the coal maceral, vitrinite, in the source rocks or other closely associated sediments. Thus, the spores change from a pale yellow through orange and brown to black, while the reflectance increases in value. These properties have been used as a measure of the maturity of the source rock, and hence whether it has or has not reached the stage of significant oil generation or gone beyond the so-called oil 'window' into the oil extinction/principal gas generation stage. The main oil generation seems to be associated with values of vitrinite reflectance in oil of about 0.5 to 1.2 per cent. For spore coloration the orange and brown colours mark the main oil generation zone, and dark brown the dry gas stage. The onset of the main oil generation phase may be associated with a reflectance value which varies to some extent with the nature of the kerogen, while some kerogens are described as gas-prone—they generate gas, but no substantial amounts of oil.

A third means of assessing the maturity of source rocks is by the pyrolysis of a small amount of the source rock. The temperature is raised rapidly and the material vaporized or formed by thermal breakdown of the kerogen is passed through a detector which records, on a temperature base, peaks representing these two bursts of volatile material. To a first approximation the peak at the lower temperature represents oil already generated; the peak at the higher temperature indicates oil capable of being generated at adequate maturity.

A source rock must contain organic carbon, but a measurement of the organic carbon content, a simple operation, is in itself not adequate to show that the rock has given or is potentially able to yield oil or gas; the organic carbon may be dead carbon, the kerogen may not be oil-prone, or it may be oil- or gas-prone, but immature. Recognition of these points is important in exploration. An exploratory well may fail to find oil or gas for various reasons; there may be no reservoir rock, a reservoir rock but no trap; no source rock or a potential source rock that is not sufficiently mature to provide oil or gas for a trap, or an over-mature source rock. Examination of samples of source-rock type material from a well may answer important questions with regard to the hydrocarbon potential in the area. The answers may suggest that at the depths in question oil

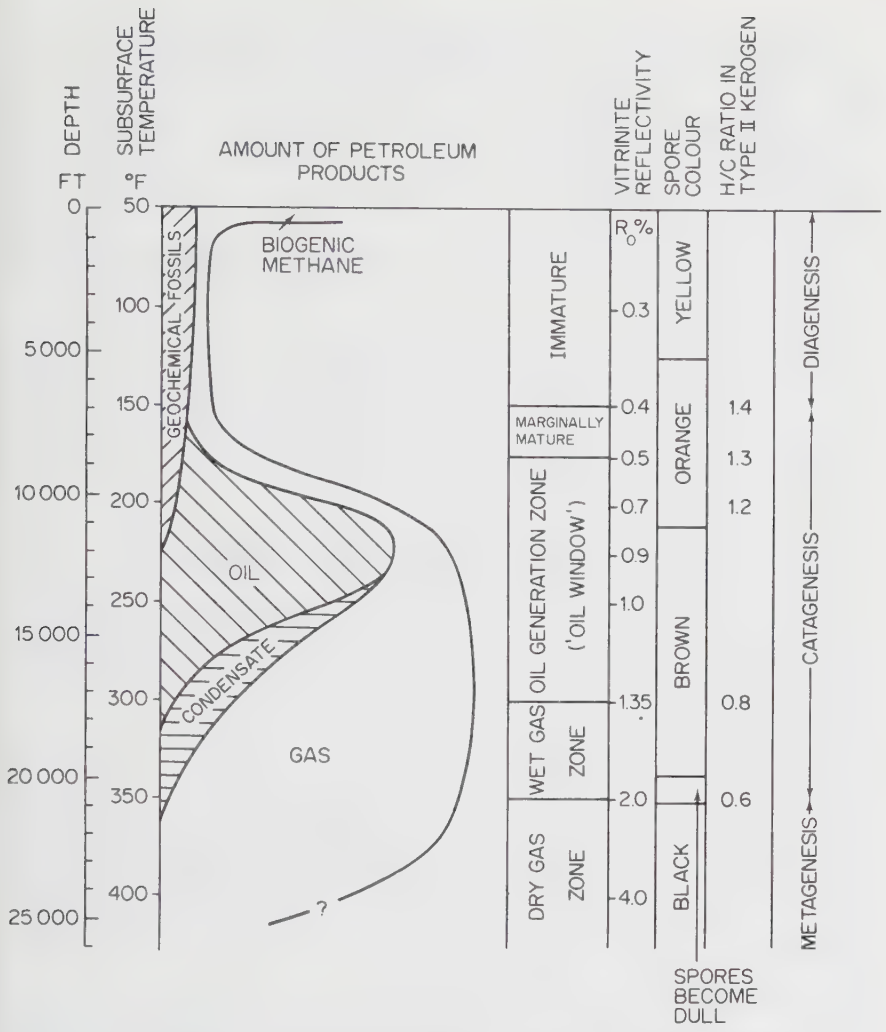

FIG. 7. Petroleum formation and evolution, and some associated factors.

cannot be expected unless it has migrated upwards from a decidedly deeper source rock, or that deeper wells are needed for adequate tests. On the other hand they may indicate that gas rather than oil accumulations are to be expected.

It has been suggested that an effective oil source rock generates 10–40 brl of oil per acre ft (0.0013–0.0052 cc/cc) for each one per cent of organic carbon. This is approximately 500–2000 ppm by weight.

Evolution or Original Differences?

It is now generally accepted that crude oils evolve, and that there is a progression over time and under the influence of heat towards lighter mobile

material. Many years ago L. G. Weeks suggested that the type of oil is dependent on the position in the depositional basin, and that the oils become lighter in going basinward in any horizon. It certainly seems likely that the depositional environment would determine the type of oil formed and could exert an influence on the character of the oil for a long time, even though there is evolution. However, the history of basins is sometimes complex, and when this is the case vertical and age sequences may differ from the simple pattern which might be indicated by Weeks' statement.

H. D. Hedberg has noted that high-wax-content crudes largely have certain associations, for example in sand/shale sequences as opposed to carbonates; commonly with coals or other highly carbonaceous beds; non-marine or waters of less than normal marine salinity; continental, paralic, or near-shore environment; low sulphur content; Devonian to Pliocene in age. The parental organic matter may therefore be in part terrigenous or from aquatic organisms living in waters of lower salinity than normal marine environments.

Deeper burial with the formation of more light hydrocarbons, or via higher pressure forcing more light hydrocarbons into solution in the crude oil, can cause the precipitation of asphaltic matter from the crude.

Contact of crude oil with meteoric waters permits water-washing whereby the gasoline fraction, especially the aromatic and naphthenic components, is depleted by solution in the water. Bacteria may be introduced by meteoric waters and may cause biodegradation of the crude, mainly by removing the n-alkanes. These two processes result in the remaining crude oil becoming heavier than the oil which undergoes modification.

Migration and Accumulation

In view of the very small quantity of hydrocarbons and the small amounts of organic matter found in recent and ancient sediments thought to be possible source rocks (Tables IV and V), it is apparent that there must be some process of concentration to form commercial hydrocarbon accumulations in which oil or gas locally occupies as much as 80 per cent of the pore space in the reservoir

TABLE IV
Occurrence of Hydrocarbons in Sediments

Area	Depth	Concentration of hydrocarbons in recent sediments (ppm)
Pedernales (Venezuela)	20 to 160 ft*	33–62
Gulf Coast: Grande Island		20–95
Pelican Island		31–50
California		180
Lake Mendota, Wisconsin	0 to 27 in†	120–350
Trout Lake, Wisconsin		270–285
Cooking Lake, Alberta		945‡

* A. L. Kidwell and J. M. Hunt.
† S. Judson and R. C. Murray.
‡G. W. Hodgson.

TABLE V
Hydrocarbons and Organic Carbon in Sediments

	Organic carbon content (% wt)	'Hydrocarbon' content boiling above 325°C (ppm)	'Hydrocarbons' / Organic carbon
Recent sediments	0.3–3.4	20–140	0.0014–0.01
Ancient sediments	0.76–5.8	67–3032	0.0042–0.113

Based on data assembled by Blumer and by Philippi.

rock. Furthermore, such a process could place the accumulation normally in the highest available part of the reservoir rock. The process of emplacement and concentration of the hydrocarbons in the reservoir rock is referred to as migration and accumulation.

If the source rock differs from the reservoir rock it is convenient to consider two stages in the process:

1. Movement from the source rock to the reservoir rock, and
2. Movement and segregation within the reservoir rock.

The first stage has been labelled primary migration and the second stage secondary migration.

As yet there is no certainty about the exact state of the hydrocarbons in the source rock *in situ*. The possibilities are free globules, hydrocarbons in 'solution' in the pore water, or adsorbed on organic matter or on inorganic mineral matter. Commonly it has been assumed that they occur as minute globules in the source rock, and there have been claims that primary migration is caused by buoyancy, interfacial tension, or water flow. However, buoyancy and interfacial tension seem improbable as the agents when due note is taken of the likely circumstances. It is less easy to exclude the possibility that primary migration is associated with water flow, although it may not necessarily be caused by water flow.

Should a source rock be fine-grained, as seems to be the general case, it will be subject to compaction, since newly deposited fine-grained rocks have a high ratio of water to mineral matter, but after burial to a considerable depth the water/mineral matter ratio becomes quite small. The water is squeezed out of the fine-grained rock (Table VI). If the squeezing causes the movement of the hydrocarbon globules they might leave the source rock along with the water, without strictly being carried by the water flow.

Transport *by* water would become less easy as compaction proceeds since the amount of water available diminishes as the rock becomes more deeply buried. Fluids expressed by compaction will ultimately, if not initially on all occasions, move upwards through the sediments. The exact path is determined by the geometry and permeabilities of the beds to be traversed. The flow will be distributed in accordance with the resistances met, and a highly permeable bed, such as could act as a reservoir rock, will in a sense focus some of the flow if it is inclined or unevenly covered by low-permeability beds.

A range of mechanisms for primary migration have been proposed. There are two main groups: migration in solution, and migration as a separate phase,

TABLE VI
Water Content of Clays

Depth (ft)	Porosity (% vol.)	Water content relative to the probable initial water content*
0	80	1.0
20	64	0.44
40	60	0.37
80	52	0.27
120	45	0.21
200	32	0.12

Based on data obtained by A. L. Kidwell and J. M. Hunt for the clays of the Pedernales area.

* The water now in the pores of a clay need not at all depths be water which was included at the time that the given portion of the sediment was laid down.

of which there was brief mention above. The first group must involve dissolving the hydrocarbons in water in the source rock, their movement by diffusion or by bulk flow of the water, and their release in the reservoir rock. Both true solution and solubilization in water containing colloidal electrolytes have been considered. Solubility is extremely low in the former case, but does rise progressively more rapidly at higher temperatures. Upward flow into zones of lower temperature would cause gradual release from solution, but there would not be discrimination, and release could occur in non-reservoir rock as well as in reservoir rock.

In the case of solubilization salting-out, or dilution leading to a drop in the colloidal electrolyte concentration below the critical level at which the micelles responsible for 'dissolving' the hydrocarbons can exist, would be more likely in a reservoir rock than elsewhere. There have been various suggestions for organic substances that could act as colloidal electrolytes. Substantial amounts would be needed. However, they would probably be subject to breakdown on heating, and so would disappear, releasing solubilized oil, not necessarily only in reservoir rocks.

For migration as a separate phase some of the earlier ideas made use of the concept of relative permeability for two-phase flow in a porous medium, the source rock. For two immiscible fluids at low saturations a fluid is immobile; however, above such saturations its mobility increases, slowly at first, and then quite rapidly with increase in saturation. Progressive loss of water during compaction and further oil formation would favour oil flow as the depth of burial increased. Also it has been suggested that some of the water is bound to the mineral matter, thus enhancing the proportion of oil in the mobile fluids. A partial offset to this at one stage of burial is water release by clay mineral transformation, a feature which could be beneficial for migration in aqueous solution, with oil formation a comparatively late process.

The organic solids (kerogen) in source rocks may well show some segregation along bedding planes; they are unlikely to be uniformly disseminated in the rock. Should there be continuity on the bedding planes, it has been postulated that oil could migrate via the kerogen acting as a wick. However, means for release from the wick do not seem to have been proposed.

In recent years it has been suggested that microfractures in the source rock would facilitate the flow of oil, but it would also seem that if there is water still potentially available for expulsion its flow would also be aided. (Microfractures may be as narrow as a 30 to 100 Å, according to Neglia.) A coherent primary migration mechanism involving microfractures has been outlined by J. A. Momper. The basic concept is that in oil generation there is an overall potential increase in the volume of the organic components in the source rock, i.e. the volume of kerogen before oil generation is less than the volume of residual kerogen (or 'dead' carbon) plus generated hydrocarbons. If flow cannot take place this potential increase in volume leads to a rise in pressure which creates microfractures. The fractures permit pressure release, some fluid (claimed to be oil) is expelled from the site of oil formation, and the fractures then close, only to be reopened by further oil generation from the kerogen. According to this hypothesis oil expulsion is an intermittent progressive process. An essential element in the mechanism must be no permeability in the source rock, or at least such a low permeability during the oil generation phase, that any fluid bleed-off does not offset the pressure build-up associated with a potential increase in the volume of the total organic matter. Momper does not appear to have discussed the matter of whether at the oil generation/expulsion stage there is absence of potentially mobile water, i.e. that the possibility of compaction no longer exists, in the sense of fluid expulsion by reason of the load of overburden, irrespective of whether the flow in such compaction is via normal intergrain pores or microfractures.

Many years ago in discussing oil migration being associated with the expulsion of compaction fluids, it was pointed out that late oil generation would lead to less oil being moved out of the source rock than for early oil formation. Continuing changes in the source rock whereby more oil is formed, or already formed oil is broken down to gas, make it difficult to examine various matters and thereby to demonstrate particular points. Oil in transit will be at levels containing organic matter not in detail responsible for its generation.

Expulsion efficiencies of 5 to 10 per cent have been mentioned for the removal of oil from source rocks.

In association with the above oil migration mechanism it has been suggested that gas migration is by diffusion, and it may be noted that a considerable number of years ago Roof and Rutherford concluded that the rate of diffusion in aqueous solution is enough to explain gas accumulations. In this instance release from solution would be determined by pressure drop, and again would not be a function of lithology. However, should free gas be associated with oil in the source rock, i.e. be in excess of the amount that could be dissolved in the oil and water, it would presumably take advantage of open microfractures and move with the oil or water.

On balance in the light of present knowledge oil migration as a separate phase seems to be the more likely condition. Microfracturing would facilitate movement. It should be noted, however, that it has also been suggested that aquathermal over-pressure can develop, leading to microfractures, provided that zero or very low permeability exists, as mentioned in an earlier paragraph.

If, as a result of primary migration, minute oil and gas globules enter or develop in a reservoir rock, their subsequent behaviour will depend on a number of factors. Should they be at the top because of locally-downward

movement from the source rock, they may be expected to stay near the points of entry, where they will be joined, with coalescence, by further globules. Should they be at the bottom of the reservoir rock, and if they are sufficiently small, they will rise by buoyancy to the upper boundary of the rock where they will be joined by others, again with coalescence; alternatively, if they lodge near the bottom, again they will be joined by other globules. When an oil mass or a gas mass of suitable height has been built up it will be capable of rising by buoyancy within the reservoir rock, and this movement could be aided by favourably directed water flow. The necessary height is fixed by the pore and the pore throat sizes, densities of the hydrocarbons and water, the interfacial tension and the direction and vigour of any water flow. Oil and gas will therefore tend, in general, to move to the locally highest available part of the reservoir rock, and the paths followed will be highly selective.

In a flat-lying reservoir rock the oil and gas will remain in the area where they entered the rock during primary migration, in the absence of lateral water flow. The extent of segregation will depend on a variety of circumstances. Should the reservoir rock be or become tilted there will be greater chances of secondary migration, because the buoyancy factor due to overall height of oil or gas masses will be increased. Lateral and upward movement to give greater local accumulation then results.

When the rocks are flat-lying, and the hydrocarbon columns are comparatively small in height, because of little lateral movement, quite small changes in pore sizes in the reservoir rock will hold back the oil and gas.

So far, in discussing migration and accumulation, no reference has been made to the reason for the oil and gas not moving upwards from the reservoir rock into the fine-grained (and finer-pored) cap rock. In order to force an oil or gas globule of diameter greater than the water-filled pores of the cap rock into that rock the globule would have to be distorted. This distortion is resisted by interfacial tension. There is, of course, no absolute bar to passage into the cap rock, but a critical pressure difference must be attained before entry is possible (Table VII). When there is a large difference in capillary pressure between the reservoir and cap rocks the critical pressure difference is high and would require the existence of a very tall hydrocarbon column in the reservoir rock for penetration of the cap rock to occur.

Structures develop and change over time. A structure can trap oil or gas only when it lies in the path of migration. Hence traps which develop after the hydrocarbons have migrated past their position will be barren. Also the initial accumulations need not be permanent, for tilting may reduce the effective

TABLE VII
Capillary Pressure and Pore Size

Pore radius (cm)	Capillary pressure (30 dynes/cm interfacial tension) (dynes/cm^2)
0.1	600
0.01	6 000
0.001	60 000
0.0001	600 000

storage volume of a structure as a trap. Alternatively, reduction in depth of burial, with drop in pressure releasing gas from solution in the oil, may cause the volume of the hydrocarbons to exceed the storage capacity of a trap; excess hydrocarbons would move from the trap to escape or to accumulate elsewhere. Oil and gas accumulations, because of their mobility and ready response to changes in the conditions, must be looked on as probably the most transient of mineral deposits.

Relatively small lenses and up-dip wedge-outs arising in the deposition of reservoir rocks provide traps as soon as they are covered. The former localize accumulations permanently, provided that the seal remains intact. The latter, although they give early trapping, need not be the site of an accumulation for ever, because suitable tilting could later cause hydrocarbons to move from the early site of trapping, when the reservoir rock is extensive compared with the amount of hydrocarbons present.

Early accumulating gas would be bulky, because of the low pressure conditions. Increase in depth of burial would drive more gas into solution in any associated oil, and vice versa (Fig. 8). Natural gas is much more soluble in oil than in water.

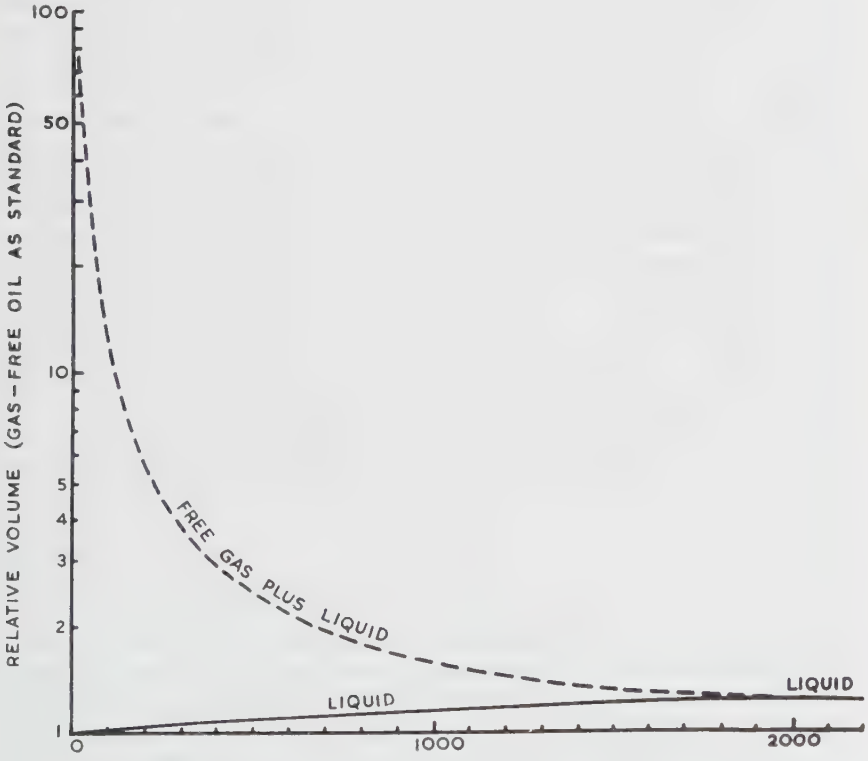

FIG. 8. The curves show the behaviour of a given gas–oil system when the pressure on it is varied. Change in depth of burial of a hydrocarbon accumulation would alter the pressure on it, thus causing volume changes comparable with those shown, although modified to some extent by the changes in temperature which would accompany the changes in depth of burial.

Inclined fluid contacts can arise in several ways, one being lateral changes in pore size in the reservoir rock, another being water flow past the accumulation. Evidence of water flow is afforded by the existence of pressure differences in the water in the reservoir rock at a given datum plane. With water flow the hydrocarbon accumulation is displaced laterally and vertically with reference to the position which it would occupy in the absence of water flow, and consideration has been given to such possible displacement in searching for oil or gas in some areas. The extent of displacement depends on the rate of water flow, the density difference between the hydrocarbon mass and the water, as well as on other factors.

Seepages

Leakages of hydrocarbons from accumulations are referred to as seepages or shows. They can take place in two ways: (a) from exposure of the reservoir rock as a result of erosion; (b) from a buried reservoir rock via a fault or joints which provide avenues for movement through the cap rock. Sometimes, although the reservoir rock is exposed, asphaltic matter from the crude clogs the rock pores at the surface, thereby greatly reducing the rate of loss of oil. Some oilfields have been developed down-dip from places where asphaltic matter has formed a seal for an outcropping rock. Oil-impregnated rock and no obvious oil flow are the features of many shows.

Seepages vary in size and vigour, and the amount of hydrocarbons seen will depend on conditions at the surface, as well as on the nature of the oil. If the seepage is on a slope the material will flow away from the point of issue, as well as be lost in part by evaporation. It may be washed away by rains or streams. Under dry conditions there may be impregnation of the soil. When escape is into a hollow the less volatile components of the crude oil will accumulate, and if sufficient amounts are able to collect in the case of an asphaltic crude the result is an asphalt lake.

Gas escapes are best seen when they occur under water. There are also cases in which gas along with water moves through clayey rocks, forming a gas-charged mud which issues at the surface to give a mud volcano.

Seepages obviously show that an area has been suitable for the formation and accumulation of hydrocarbons. Only detailed study can indicate whether the escape is likely to represent an early or a late stage in the loss of the hydrocarbons.

BROAD PATTERNS IN OIL OCCURRENCE

In some oilfield provinces a broad pattern can readily be recognized when the distribution of the fields and their nature are studied. A major unit commonly discernible is the geosyncline, a belt in which there has been much sedimentation and which typically evolves to a large asymmetrical structural basin (Fig. 9). On the gentler side, ancient rocks, in some cases part of one of the major shields, are seen to outcrop; they also underline the sediments. The structures in the sediments on this side are gentle, and faulting is common in some belts, especially along the hinge line where in a regional sense the gentle platform region gives way to the main sag of the deep basin. On the more

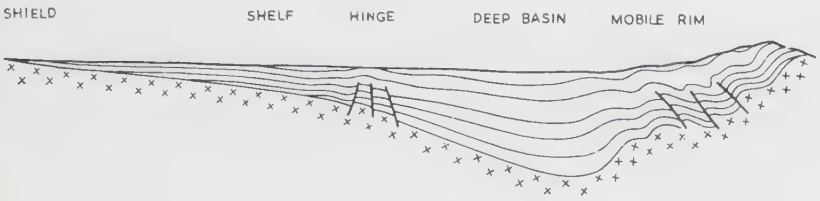

FIG. 9. Simplified diagram depicting the main features of a geosyncline as seen in vertical cross-section. The vertical scale is greater than the horizontal scale. The length of the section could be several hundred miles, and the thickness of the sediments over the basement (marked by crosses) in the deepest part could be of the order of 5 to 10 miles.

disturbed side there are foothills and mountain ranges; strong folds, faulting, and overthrusting occur. The present geological pattern is the consequence of developments which have taken place over a long period of time. These developments involve not only structure, but also have had certain types of sedimentation and sedimentary patterns associated with them.

The thickness of the sediments formed is less on the shield or shelf (platform) side than elsewhere. The maximum thickness lies between the shelf side and the mobile rim where the strong structures have developed.

Examples of this broad pattern can readily be seen as follows: in the Middle East—the Arabian shield, the area of the Tigris–Euphrates valley and then to the north-east the Zagros range of mountains running north-west–south-east; in Canada—the Canadian shield with the plains area to the west and south-west, and then the Rocky Mountains to the west, running roughly north–south; in northern South America—the Guyana shield, the Orinoco valley to the north and then the Venezuelan Andes still farther north, running east–west.

Because of a tendency for certain types of trap to be commoner in some parts of a geosyncline than in others, there has frequently been a spread in discovery activity over time from one part to another. Thus the folds of the foothill belts commonly attracted attention at an early date, but it must be recognized that the precise reasons which lead to oil exploration activity are complex, and include the state of development of geological knowledge and techniques, as well as the extent to which natural processes have led to the revelation of the occurrence or probable occurrence of oil in an area. There can also be geographical and political reasons. Surface geology is commonly a good guide to the location of anticlinal traps and fault traps; deep erosion and faulting are responsible for seeps in some places, drawing attention to oil having been formed and accumulated in the area.

On the shield side the gentle structures have in some cases been less easy to detect by surface geological mapping, and other techniques have proved helpful. In the centre the greater thickness of sediments has made thorough investigation of the oil possibilities a difficult proposition.

There are other types of areas of sedimentation which can provide oilfields. The underlying basement is more rigid than that under the geosynclines, and this leads to some differences in structures and other features.

In 1955 G. M. Knebel and G. Rodriguez-Eraso analysed data for 236 major oilfields (fields with estimated recoverable reserves in excess of 100 million barrels each) in the Free World. In terms of recoverable oil these fields

represented 82.5 per cent (217 000 000 000 brl) of the oil reserves in the Free World found up to that date. The other reserves are spread among many thousands of smaller fields.

The results for the Free World are summarized in Table VIII, and the data for the Middle East are also given separately in order to show the influence of such exceptional fields on the overall picture.

TABLE VIII
Oil Reserves and Geological Factors

	Reserves—10^9 brl	
	Free World	Middle East
Position in structural basin		
Mobile rim	46.3	29.4
Deep basin	24.8	11.4
Hinge	109	99
Shelf	29.2	
Others	7.7	
Lithology of reservoir rocks		
Sand, sandstone	128.1	68.9
Limestone, dolomite	87.3	70.9
Fractured shales, igneous and metamorphic rocks	1.6	
Type of trap		
Anticline	173.5	139.8
Fault	2.7	
Unconformity	6.1	
Reef	5.2	
Other stratigraphic	15.8	
Combination	13.7	
Type of oil		
Paraffin-base	18.8	
Mixed-base	163.3	139.8
Asphalt-base	34.9	
Age of reservoir rock		
Plio-Pleistocene	7.6	
Oligo-Miocene	62.3	36.3
Palaeocene-Eocene	13.1	5
Mesozoic	114.3	98.5
Palaeozoic	19.7	

Although in some instances the precise classification may be debatable, the tabulations as a whole may be expected to be representative of the characteristics of the major fields known at that time.

About thirty years ago some interesting tabulations were published, in which production and geological data for some 7600 oil and gas pools in the USA were summarized (*Journal of Petroleum Technology*, 1950). The information related to the position at the end of 1949 and during that year, and was for the more important accumulations. Because of the necessarily contracted form in which the data were presented there are clearly approximations, and also limitations in the amount of detail possible. However, Table IX gives the results of an attempt to summarize some of the information in terms comparable with those

TABLE IX
Geological Factors and Oil and Gas Pools

	Percentage of fields or pools		
	USA*	USA major oil and gas fields†	Free World major fields‡
Type of trap			
Anticline	65.4	77.8	58.2
Fault	5.2		7.8
Unconformity	0.7	10.8	6.0
Reef and other stratigraphic	10.2		16.1
Combination		11.4	11.9
Lithology of reservoir rocks			
Sand, sandstone		66.8	61.7
Limestone, dolomite		31.9	32.0
Fractured shales, igneous and metamorphic rocks		1.3	6.3

* Based on information in *Journal of Petroleum Technology*, 1950.
† From data assembled by M. T. Halbouty, *Bull. Am. Ass. Petrol. Geol.*, 1968, **52** (7), 1115–1151.
‡ From compilation by G. M. Knebel and G. Rodriguez-Eraso, *Bull. Am. Assoc. Petrol. Geol.*, 1956, **40** (4), 547 561.

used by Knebel and Rodriguez-Eraso, in order to find how far the relative numbers of accumulations of given types are comparable for the pools in a substantial area with corresponding figures for the major fields of the Free World. The table also includes segregated information on 305 major USA oilfields and gasfields. (A major gasfield has reserves of more than 1×10^{12} ft^3 of gas.) The data on which the tabulations are based do not allow the comparison to be made in terms of reserves.

Exploration for oil and gas is being actively pursued. Offshore areas have been investigated for only a relatively short time, and there are other areas which must be deemed to be in the early stages as regards oil development. In some areas deeper probing in search of oil seems justifiable.

Of the world total land area of 55 768 000 sq. miles, Weeks has classed some 18 500 000 sq. miles as basins. The offshore shelf and upper continental slope, with water depths not exceeding 1000 ft, have an area of 10 763 000 sq. miles, of which 6 170 000 sq. miles is as basins; 1 845 000 sq. miles appears to be favourable for oil occurrence, and 4 325 000 sq. miles has submarginal oil prospects or is not commercially attractive on present information. It was stated in 1966 that offshore oil reserves were estimated to be 18 per cent of the Free World's oil reserves, and that the offshore daily output was 16 per cent of the Free World production. In the first six months of 1981 in the Free World, excluding USA, the average daily oil output of offshore fields was about 28 per cent of the total production.

In spite of the fact that the major basins of deposition which have developed over time will have had certain features in common, there may well have been differences in the relative amounts of oil formed, and in the relative numbers of oilfields created with given characteristics. In addition there are the matters of preservation and accessability, for oil accumulations have undoubtedly been

lost by seepage, and various factors will impose limits to the effort which will be applied in searching for new fields. Hence, with very substantial amounts of oil probably remaining to be found, it is not possible to be certain that the present picture, which may be imperfectly revealed by the tabulations, is a close representation of the picture which will ultimately be developed.

WHERE NEXT?

Offshore drilling and completion techniques have developed to a stage at which it appears technically feasible for operations to be carried out in water of much greater depth than has so far been tackled. The costs would be high, but with suitably large objectives wells in deeper water could become economically practicable. The present continental shelf activities could therefore be followed by operations on the continental slope, provided that the geological conditions are satisfactory.

The concept of continental drift, irrespective of the precise fundamental mechanism envisaged, leads to speculation on the extent to which the continental shelf and slope are dependent on sedimentary build-up and build-out, and how far out to sea sedimentary rocks and structures pre-dating the start of separation of the continental blocks extend. Heezen considered that the outcrop patterns observed on the upper continental slope are controlled by the interplay of depositional processes on the shelf and erosional processes on the slope; that the slope owes its location and primary origin to deep-seated fundamental faults. Uchupi and Emery's interpretation of seismic profiles run off the east coast of USA was that sedimentation during the Tertiary exerted a far greater control than erosion and faulting on the present form of the continental margin; it did not establish the origin of the continental slope, since the Tertiary sediments were believed to have built on and extended seawards a previously existing continental shelf and slope. Patterns of deposition indicated in the vicinity of the slope were not the same on all the profiles. Fig. 10 shows a profile of the continental margin off the eastern coast of the USA.

The early stages of the separation of the continental blocks could be associated with different conditions and types of sedimentation from those of times when a wider and perhaps deeper body of water separated the land masses.

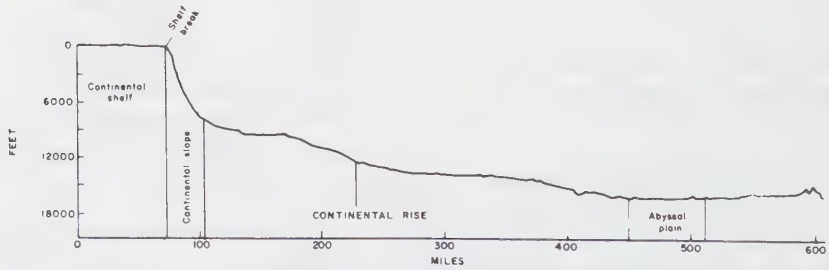

FIG. 10. Profile of continental margin off eastern USA. (After B. C. Heezen, The deep sea, pp. 235–288, in *Continental Drift*, S. K. Runcorn (Ed). New York and London, Academic Press, 1962.)

On geological grounds alone the neighbourhood of the continental slope may be expected to present special challenges. Limited sampling has shown the presence of organic matter and hydrocarbons in recent sediments on the slope. It should also be noted that just as shallow-water sediments can be buried by great thicknesses of other sediments, geological processes can lead to such sediments becoming covered by deep water in addition to sediments. Consequently, deep water may in places be underlain by rocks in which oil and gas can be formed, provided they contain suitable organic matter and have also, by burial, attained temperatures appropriate for the generation of hydrocarbons. In recent years holes drilled in the JOIDES programme have found evidence of oil or gas deep in the Gulf of Mexico, on the Shatsky Rise in the West Pacific, in the Balearic and Tasman Seas, and on the Vøring Plateau off Norway. Two kilometres of sedimentary rocks has been indicated in the Rockall and Hatton Basins, 5 km in the Rockall and Porcupine Troughs, and 2 km under 4000 m of water off Somalia.

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2

Exploring for Oil and Gas

By N. L. FALCON

INTRODUCTION

The fourth edition of this book was published in 1973, the year in which the era of cheap oil ended. This began to disturb the world economy causing governments and other organizations to face up to the problems of the long-term energy future. The oil exploration effort increased, and research and development in all relevant technical fields were stimulated. The increasing hostile environments of prospective offshore areas led to increasing costs of exploration and development, far beyond general inflation. Outstanding developments in exploration technology in the last decade have taken place in the engineering, geophysical, and geochemical spheres, and geological work has increased owing to the availability of new electronic tools and information from below seas and oceans. A noteworthy change has also been increasing collaboration between academic and industrial workers.

The previous chapter should have made it clear that hydrocarbons in commercially significant quantities are found in sedimentary rocks; the few exceptions are explicable by contiguity. This primary fact is supported by factual data from over 100 years of exploration activities throughout the world, including the drilling of millions of boreholes. The negative information that oil and gas are not found in significant quantities in igneous or metamorphic rocks not contiguous with sedimentary rocks is also confirmation of the sedimentary origin of the hydrocarbons in which the oil industry is interested.

Although many of the details of the processes of oil formation remain speculative, it is the belief of oil geologists that the hydrocarbons for which they search have been generated from organic material deposited with the sedimentary rocks. If this is regarded only as a working hypothesis by some scientists outside the industry, it has been very well tested, and certainly cannot be replaced. In any case, economic extraction can only be achieved from rocks with adequate porosity and permeability which normally are confined to sedimentary rocks.

It is clear therefore that the basis of oil and gas exploration must be knowledge of the geology of sedimentary rocks, their nature, mode of origin and geological history, because it is in these that the hydrocarbons have their being, migrate, and accumulate. As all sedimentary rocks, except those of an organic or chemical origin, have been formed from the products of the weathering and erosion of older rocks, a broad knowledge of geological processes is required to develop insight into the many problems involved in exploration, particularly those concerned with the geological time factor, a fourth dimension quite outside the range of normal thinking.

Geology is concerned with many facets of the study of the earth's crust. It must use knowledge of the present natural environment and its energy phenomena to interpret the records of the rocks in terms of past geological

processes. As all energy phenomena of the atmosphere, land, and oceans are relevant to these processes a wide background knowledge of the physical, chemical, and biological sciences is necessary for the petroleum geologist if he is to give the best advice to the other members of the exploration team, the management, the geophysicists, and the most essential drillers.

Geological research proceeds by the collection of observed data and the study of these data by the alternate use of deductive and inductive reasoning. Geology can never be an exact science because of the imperfection of the geological record. Although quantitative physical measurements made with sophisticated modern apparatus are being used more and more in geological research and for practical exploration purposes, this must not be allowed to obscure the fact that exploration is concerned with those areas where factual data are either scarce or virtually non-existent. Much speculative thinking is necessary.

In considering the educational requirements of the petroleum geologist it is useful to look at medicine, another inexact science. No matter what branch of medicine a doctor subsequently practises, he spends a number of years studying background scientific subjects and learning about the human body as a whole, and its processes. He is obliged to learn the anatomy of the body by dissection. All this assists diagnosis. Likewise the petroleum geologist should have a broad background of basic science and learn as much about the earth's crust as possible, dissection being replaced by field work. Unfortunately, field work tied to specific exploration operations is becoming hard to achieve. A broadly based academic course of geology before specialization is imperative. Specialization can follow later, perhaps within industry. To economize by early specialization, or by concentrating on practical work in industry to the neglect of theory, may create useful technicians but is unlikely to produce geologists with the insight necessary for the wider tasks.

There is no direct method of finding oil and gas, although recent improvements in geophysical techniques (seismic reflection) can now suggest the presence of gas in suitable reservoir rocks. Oil and gas at depth are found by drilling expensive boreholes, at greatly increasing costs as exploration environments become physically more hostile. The history of oil and gas exploration is a series of detective stories, and the philosophy that of the hunter. The aim of this chapter is not to teach geology or to go into technical details of methods but to give a broad outline of the procedure and the thinking behind it. Exploration for solid hydrocarbons is not discussed; being non-mobile their extraction is more akin to mining.

INITIATION

Oil and gas exploration is a highly speculative form of investment which can be carried out efficiently only by wealthy organizations with a desire or need to explore. The motive is invariably profit, direct or indirect. It is the task of the petroleum geologist to serve those who wish to explore by selecting the promising areas. His work is a specialized type of scientific research, differing from the research of academic colleagues by having a limited, utilitarian objective. The minimum work necessary to satisfy the objective will be authorized. Many data of interest and direct use in hydrocarbon exploration

are obtained from the work of geological surveys and academic researchers, and in return much information of interest to others becomes available as a by-product from hydrocarbon exploration.

CONCESSIONS

In the early years of the petroleum industry boreholes were drilled in the neighbourhood of oil seepages, by private arrangement with landowners, with or without geological advice. Many shallow fields were found in this way. Increasing experience showed that many seepages and oilfields tended to arise from porous strata on structural highs. Soon geological studies became a wise adjunct to concession hunting and borehole location. The petroleum geologist gradually became a key figure in the selection of exploration areas, sometimes backing his judgement by taking a personal financial interest in concessions, selling shares to partners to finance future operations. This procedure is dependent on private ownership of petroleum rights. In most countries today petroleum ownership is vested in governments which issue and control permits or licences to explore, and exploit, discoveries. Areas to explore may now be selected by governments (advised by geologists) with or without pressure from industry. Individual licences to explore within these areas, usually in the shape of rectangular blocks, are granted to exploration organizations on conditions laid down by government. The whole concession-obtaining process has become the responsibility of specialized legal and concessions departments. Concessions or licences are usually granted in two phases, exploration and production. During the former, operators evaluate their concession areas, perhaps discovering and starting production from some oil or gasfields. During the latter, areas held are reduced in size but maintained for a longer period, and appraisal continues, but the main work should be the exploration of discoveries.

PROSPECTIVE AREAS—GEOLOGICAL CRITERIA

The essential general condition for an oil or gas prospect is a thick succession of sedimentary rocks, preferably deposited in a marine or estuarine environment. This is usually found in basins or troughs below which the earth's crust has sagged gradually over a long period of geological time, allowing the accumulation of large amounts of rock debris as sand, mud, or calcareous deposits of organic origin, such as coral reefs, or chemical deposits such as salt, anhydrite, or gypsum. These sedimentary rocks, to be of exploration interest, must contain 'source beds' in which oil or gas can be generated, reservoir rocks, and cap rocks, and their geometry or structure must have been suitable throughout their geological history for the accumulation of hydrocarbons by migration, and for providing hydrocarbon traps. The most promising reservoir rocks are clean, well-sorted sandstones, detrital limestones, porous dolomites or reef limestones. The most efficient cap rocks are impervious chemical deposits or compact mudstones or shales. The most simple structure is the unbroken dome or anticline. Major oilfields are usually associated with large structures in thick deposits of sediments.

These elementary desiderata require a great deal of subsurface geological

knowledge to establish. It is in the nature of oil and gas exploration that most of the data required for the accurate assessment of prospects become available as an area is explored, as hindsight. In the early years of oil exploration the selected prospective areas were shallow prospects with a reasonable number of rock outcrops where further exposures could be created by inexpensive excavation. As exploration went deeper the useful outcrop data lessened. Prospects became more conceptual than visible. More and more today they tend to lie below areas covered by alluvium or water, forcing the appraising geologist to extrapolate data, or to obtain the assistance of indirect geophysical methods of investigation, or even to advise the drilling of expensive information boreholes before adequate advice can be given or the exploration programme justified.

Experience and theoretical reasoning suggest that oil formation in commercial quantities requires some minimum overburden thickness to provide the source material, temperature, and pressure necessary for oil formation. The figure of 5000 ft sometimes used is quite arbitrary. It is known that oil has been formed in recent sediments at a depth of a few hundred feet. As everyone knows, methane is formed very near the surface at the present day as 'marsh gas'. The temperature required for oil formation cannot be specified. The temperature recorded in actual oil accumulations varies considerably, as do the temperature gradients in the rocks. In some fields temperature in the oil can be as low as 80°F, but in others it may be as high as 400°F. Clearly there must be some maximum temperature beyond which some degree of destructive distillation of oil must occur, favouring gas at great depths, but with normal temperature gradients this will be well below present normal drilling depths. Commercial oil accumulations have been found at depths from a few tens of feet (outcropping oil sands sealed by bitumen) to over 20 000 ft. Great depths of burial increase the chances that the porosity of reservoir rocks will decrease owing to overburden pressure. Crystallization of mineral matter formerly held in solution in formation waters may do the same—unless hydrocarbons trapped early in the pore space prevent it. The thickness of sediment in which it is worth looking for oil and gas is, therefore, difficult to specify: it depends on the type of lithology and past migration possibilities. As it is not possible to know how far oil has migrated, even a few hundred feet of sediment at the edge of a basin may be worth investigation in suitable geological circumstances. Some minimum depth is necessary for the larger accumulations with high reservoir pressures to allow the overburden to maintain the efficiency of cap rocks. The greater the thickness of sediment in the deeper part of a basin the greater the opportunities for oil and gas formation. The most prospective part of a basin will depend on lithological and structural factors. As the former are rarely known at the start of exploration, attention is usually first directed to potential structural traps in an intermediate flank position, between the deeper part of a basin, where hydrocarbon is most likely to have originated, and the margins, towards which it will have tended to migrate. It is difficult to formulate a favoured pattern because of the great variability of individual basin histories.

Some of the various types of structure in which oil and gas may accumulate are shown in the previous chapter, Figs. 3 and 4. They can be formed in a variety of ways; by compaction of sediment over a rigid irregular basement; by

compressional earth movements; by tensional earth movements; by gravity sliding; by the intrusion of rocks into the overlying strata owing to density differences or compressional forces; by lithological change; by erosion and subsequent deposition. It is the task of the petroleum geologist to visualize the trap potential of an unexplored area in the light of the regional geology.

Much chemical research has been done in an attempt to determine the nature of source beds. Certain types of sediment are generally considered to be good source material, for instance dark shales with a high organic content, or dark argillaceous limestones. The tendency of recent micro-analytical work has been to show that organic matter, including proteins, is very widely distributed in all types of sedimentary rocks. This has the practical result that it is wise to assume that source beds are present in the sedimentary rock successions until proved to the contrary.

THE COMPETITIVE SYSTEM

The competitive system of oil and gas exploration has served the world well. Basically it is successful because exploration is always conducted in areas where, in comparison with the volume of rocks involved, exceedingly few geological facts are available and no single operator has the capacity to test all hypotheses. Although the basic geological principles of oil and gas accumulation are usually accepted and followed by all exploration organizations, the detailed or even general working hypotheses evolved from any collection of data by technical staffs, as a basis for actual operations, may be different. Working hypotheses depend on constructive geological imagination which comes best with experience. A number of organizations competing against each other in the field of ideas, all with the same tools available (if they can afford them) will find out the maximum about the subsurface geology of an area by drilling a number of boreholes located by differing working hypotheses. And even if a working hypothesis, or new data, must remain confidential initially for commercial reasons, the information must eventually become available to others, by exchange, sale, publication or 'leakage'. The effort put into exploration activities under the competitive system is controlled by world economics and the fiscal policies of governments.

Where few facts are known and geological possibilities are many all should be kept in mind. Action usually follows the making of an exploration case based on one hypothesis. If this proves wrong it may be difficult to persuade an operator to continue, unless higher management is already accustomed to the idea that the working hypothesis used was a choice of several hypotheses. The acceptance of multiple working hypotheses *ab initio* greatly increases the interest of all concerned and the flexibility of programmes.

LITERATURE RESEARCH

An exploration organization's intellectual interest in a potential oil or gas prospect ideally should be aroused by its geological staff, it being the main responsibility of a Chief Geologist to keep the areas appropriate to his organization under continuous review. The detailed work is usually done by Regional Geologists, who require experience and judgement for the task. As

exploration operations spread throughout the world the number of new prospects must obviously be diminished: for this reason the work of Regional Geologists tends more and more towards fresh appraisals of partly explored areas. Efforts to stimulate exploration interest, however, frequently come from other sources, inside or outside an organization. They may be activated by national, political, commercial, scientific, personal or even entirely misguided reasoning. Competent geological advice is necessary to assist senior managements to evaluate these pressures, to guide available exploration risk capital into the better geological areas.

Let us suppose that the senior management of a large organization becomes convinced that a discovery of oil or gas in a particular area would benefit the organization, directly or indirectly. The Chief Geologist of the organization, or if there is none a consultant, will then be asked for an appraisal of the area's prospects. Published geological reports and maps may show so many unfavourable factors, such as structural complexity, lack of sediments, etc., that further investigation may seem unjustified. More probably the reply will be that there may be some prospects, and a geologist is asked to assemble and study all available data, published and unpublished. This may require many weeks work. In the meantime the Chief Geologist should ask for a commercial study to be made to advise on the amount of oil or gas and the size of individual field considered necessary to make discovery economic. There is no sense in hunting mice if the real objective is elephants. The appraisal geologist, assisted by an information staff if his organization is wise enough to have one, will saturate himself with all the relevant geological data, much of it probably recorded in the maps and memoirs of the Geological Survey of the area, if there is one, or in papers published in learned journals. If he is lucky, he may find some reference to early oil exploration work, or early boreholes, and be able to obtain reports of this, perhaps by purchase or exchange. He will also consult with his geophysical colleagues to find out if geophysical surveys have been made in the area, and if so whether the results are available. When all information possible has been obtained, particular attention will be given to what is not known about the area, this being often more important in primary exploration than what is known. The outcome will be a brief report giving an opinion on the prospects of finding oil or gas in the quantities required by the economic study, with recommendations either for the abandonment of the idea or for further work. A common recommendation is for a limited field investigation to obtain more data. This may involve a brief geological reconnaissance. At this stage the appraising geologist must be visualizing the geology of the area objectively and also through his rosiest spectacles, creating imaginary geological conditions favourable for oil formation and entrapment wherever the lack of information allows him to do so within the framework of the known data, which at first sight may seem unfavourable. Let us assume that these further studies lead to a recommendation to apply for an exploration concession with a limited work obligation, say two years of field surveys followed by a deep borehole, with an option to renew the permit for a longer period with increased expenditure obligations. If this recommendation is accepted, a representative from the concessions branch will then visit the country concerned to arrange an exploration permit from the appropriate Government authority. Before this can be finalized, an exploration programme will have to be agreed, usually

expressed as an obligation to spend a certain minimum on exploration surveys plus the drilling of a minimum footage in exploration holes. The work necessary before drilling depends entirely on the nature of the geological unknowns; it may include geological surveys and almost certainly will include geophysical surveys. Few prospective areas justify all types of work, but those which may be used will be briefly described below.

GEOLOGICAL SURVEYS

During his brief reconnaissance visit the geologist will have probably hired an aeroplane to fly over the prospective area to 'get the feel of it' and to look for good rock outcrops. If there are good outcrops these must be examined in the field for factual data of use in hydrocarbon exploration. If there are relatively few outcrops, or maps are poor, an air survey may be required to provide vertical photographs suitable for intensive study.

The ground geological effort required depends entirely on the nature of the area and the exploration concept. It may be greatly assisted by helicopter and cross-country vehicle transport. It may involve detailed examination of all rocks at outcrop, measurement of their thickness, and the collection of specimens for detailed study in the laboratory of porosity, fossil content or other useful data. It is more than likely, however, that the exploration interest lies at a depth of many thousands of feet in rocks that do not outcrop in the area which is being assessed. In this case it will be necessary to look for these rocks some distance away where they are brought to the surface by structure and erosion. In water-covered areas a certain amount of data may be obtainable by divers in favourable conditions, for example a sea floor without superficial deposits, but this work usually requires specialized tools which will be referred to later. The geological survey report will almost certainly make recommendations for geophysical work or information drilling to fill in major gaps of geological knowledge. The term 'geological survey' may seem to connote the making of an immutable map record of the rocks. This is only true in a few semi-desert countries where the rocks are so well exposed that a vertical air photograph can sometimes be used in place of a geological map. In more normal circumstances vegetation, soil cover, and superficial deposits conceal much or all of the rock, and the making of a geological map is much dependent on research and interpretation. The geological map itself is a two-dimensional record. For exploration use it must contain data which will allow the surface information to be extrapolated in depth: this means contours, or relative heights of outcropping strata along selected lines for the drawing of vertical sections, borehole information, and data on the amount and direction of the slope of important rock outcrops. Most published geological maps lack some of this information. Even in developed countries the petroleum geologist may have to make his own maps, showing on them the data relevant to his purposes. For instance, official geological survey maps are coloured according to age of outcrops. In oil and gas exploration the physical nature of the rocks is as or more important than age, and special lithological maps may have to be made.

It will be readily apparent from Fig. 1 that surface geological maps may give quite erroneous ideas on structure at depth. This is because periods of sediment deposition may be followed by folding and erosion, and then more sediment

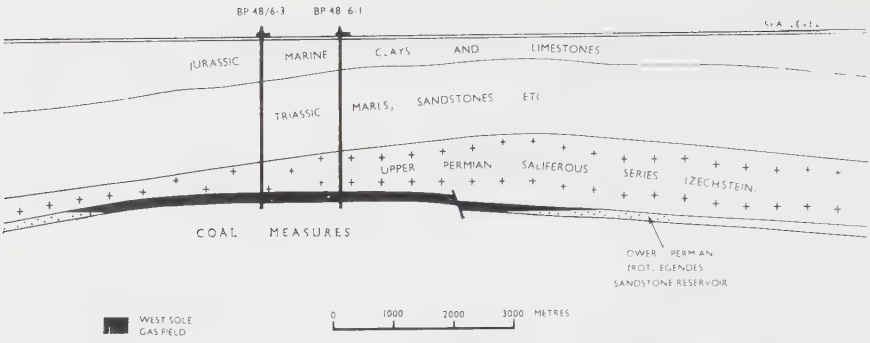

Fig. 1. Geological section through West Sole gasfield.

deposition may occur, followed by more earth movement. Units of strata may in this way be separated by an old erosion surface called an unconformity which can only be mapped in depth by geophysical surveys or boreholes. Greater complications can be introduced by low-angle faulting in structurally complex areas.

The conventional geological map is becoming less important in oil and gas exploration as operations tend to move more and more into areas without outcrops, or below water where unconformities are just as likely to occur at depth as are structural irregularities. Boreholes are almost always located today on structural contour maps drawn from seismic reflection surveys.

AIR SURVEY AND PHOTOGEOLOGY

In areas with few rock outcrops, or where available maps are poor, an air survey can be of great assistance. This may serve topographical or geological purposes, or both. The accuracy of a map made from specially flown air photographs by photogrammetric techniques depends on the accuracy of the ground control on which it is based. With adequate ground control and modern mechanical stereo-plotting equipment, accurate contoured maps can be prepared relatively quickly if the ground is not obscured by mixed vegetation. In jungle-covered country contour accuracy is decreased but nevertheless contour maps of great practical value can be prepared. For geological reconnaissance very useful maps can be made by manual plotting methods, with a minimum of ground control, or geological data can be marked directly on photographs. The great value of air photographs, which have been used in the oil industry for forty years, is that they can reveal at a glance major geological features (Fig. 13). In unfavourable terrains they may provide geological data which can only be identified by field work on the ground after laborious detailed surveys, if at all.

Photogeological work is the application of geological knowledge to the interpretation of air photographs. Topography and drainage channels are a product of weathering and erosion. They usually follow rock lithology and structure. The nature of the soil depends on the subsoil and underlying rocks which therefore may have an influence on the character of the vegetation. Major faults are often visible on air photographs, and sometimes minor fracturing of rocks and jointing. The local topography may entirely reflect the

nature of the rocks. Colour photography can be of advantage in differentiating vegetation and tracing outcrops of varying colour.

Recent developments of imaging techniques using wavelengths different from those used by the human eye are now available for obtaining certain types of geological data from air and satellite surveys. Thus radar images can penetrate thickly forested areas and through cloud cover, and infra-red images can provide data where soils and outcrops influence vegetation.

Recent enthusiasm for satellite photographs is understandable. The most beautiful satellite photographs, however, cannot by themselves reveal as much geological information as stereoscopic photographs at larger scales. They do provide a stimulating overall view of the earth's crust which can give a sense of proportion not always created by map symbols, and they may provide new structural data.

Large areas of vertical air photographs are sometimes assembled by cutting individual prints at convenient places and fitting them together as a mosaic. Interpretation of geology from mosaics requires great care and should never be done without reference to the prints under a stereoscope. This is because there are significant changes of scale owing to the varying height of the terrain. In mountainous country part of the land surface seen on one member of a stereo-pair may be invisible on the other member.

Interpretation of the features seen on air photographs is greatly facilitated by the exaggerated impression of topographical relief seen when overlapping parts of stereoscopic pairs of photographs are examined under the stereoscope. The degree of exaggeration depends on the distance covered by the aircraft between the two exposures. For vertical stereoscopic air photography aircraft flight lines must be accurately laid out to give about 30 per cent of overlap between lines, and successive pairs of photographs in each line of flight must overlap by about 70 per cent. Vertical photography for mapping is an expensive technique, best handled by specialized contractors who have the necessary ground surveyors, photogrammetric engineers, and equipment. The scales of photography can be selected to meet requirements; scale is determined by the ratio of the focal length of the camera to the flying height. Scales from 1:40 000 to 1:60 000 or smaller are useful for reconnaissance purposes, and from 1:30 000 to 1:10 000 or larger for more detailed mapping purposes.

The use of air photographs for any scientific enquiry depends primarily on knowledge of the science concerned: a knowledge of the elements of photogrammetric principles is essential but secondary. The details of the latter are the province of the professional photogrammetric surveyor. It is essential that the photogeologist should have had considerable ground experience, preferably in the type of terrain being studied. A photogeological map should either be checked on the ground for accuracy of interpretation or used by the field geologist as a working field sheet.

Photogeological and ground data should be shown on geological maps by different symbols because they are of different reliability.

SHOWS AND SEEPAGES

There is a section on seepages in the previous chapter, p. 22. The oil geologist is interested in all signs of hydrocarbons in the rocks seen at surface. Experience

however teaches him caution. The public frequently reports iron scums as oil seepages. Contamination is becoming increasingly common as world oil consumption increases. The presence of genuine seepages is always attractive, but the interpretation of their meaning is often difficult. Seepages are leaks, and in geological time leakage may have become nearly complete, whereas an absence of seepages may indicate perfect sealing. There are many seepages in the oilfield area of South-West Iran but few in the area of the Arabian oilfields. Even in country which has been much worked over by academic geologists it should be routine practice to test sandstone and limestone outcrops for bitumen residues which indicate either a former oil content or the passage of oil during migration. A test tube and bottle of solvent will be of great assistance. An obvious 10 ft oil-sand outcropping on the south coast of England was missed by several generations of academic geologists and students, because they were not hydrocarbon conscious and dismissed it as ferruginous. Seepages may give clues of underlying structure. Thus a long line of intermittent seepages in an alluvium covered area may indicate an important concealed fault. The relationship of a seepage to the oil accumulation below ground from which it has been derived requires a knowledge of the sub-surface stratigraphy and structure. Only rarely and in simple structural conditions, with the accumulation at a relatively small depth, will the path of leakage be vertically upwards; more usually it will have a lateral component owing to the accidents of fissuring and inclination of bedding. In an unconformable series of rocks overlying those which contain the accumulation, seeping oil and gas may take a very devious path to the surface.

ORGANIC GEOCHEMICAL SURVEYS

It is obvious that seepages must grade into micro-seepages which cannot be detected without instruments. Theoretically micro-seepages should be much more common than macro-seepages, and this has led to geochemical surveys to determine traces of hydrocarbons over wide areas. This involves sampling of the gas content of the pore spaces in the subsoil at some selected spacing along a series of grid lines and the determination of the hydrocarbon content of each sample. The method is little used but is sometimes tried for determining the boundaries of known oilfields, or suggesting the presence of subsidiary accumulations near known fields when the underlying geology is thought to be favourable for vertical micro-leakage. Exaggerated claims for oil finding by geochemical surveys are not uncommon: the method approaches the chimera of direct oil finding. As gas accumulations require more prefect seals to prevent loss of hydrocarbon than do oil accumulations, which initially usually contain a considerable amount of gas in solution in the oil, gas is more likely to be found than oil in subsoil pores. Here again caution is necessary because methane, the commonest product of the decay of organic matter, may be derived from vegetable matter which has not produced oil. It is the presence of higher hydrocarbons than methane in gas which is important. The use of geochemical data in the correlation of boreholes, and in inferring the possible direction of oil accumulations in unsuccessful boreholes, is referred to later.

Most exploration wells are now equipped with an automatic device which records the concentration of gas in the drilling mud. This is a useful precaution

to prevent blowouts, and can assist correlation. But care is needed in interpretation; the action of the drilling bit when grinding sediments rich in organic matter may liberate gas and cause false alarms.

ORGANIC GEOCHEMICAL RESEARCH

Identification of complex organic molecules in oils and the insoluble organic matter (kerogen) preserved in some sediments has proved beyond all reasonable doubt that these materials are derived from plant and animal remains. The different 'biological marker' molecules preserved in different stratigraphic units permit links between particular organic-rich source rocks and the oils derived from them to be drawn with increasing certainty. In all cases where there are large accumulations of oil, organically rich source rocks are to be found nearby having chemical similarities with the oil. Thus, the identification of source rocks is becoming a significant step in the exploration of an area (S.W.R.).

INORGANIC GEOCHEMICAL AND SEDIMENTOLOGICAL RESEARCH

Diagenesis of sedimentary rocks influences the formation and destruction of porosity and permeability, important criteria in speculations about oil and gas migration, and of great significance in planning production. Advances in equipment design have greatly assisted investigations of diagenesis. With scanning electron microscopes it is now possible to view in detail pore spaces only a few microns in diameter, and at the same time to determine rapidly the elemental composition of both original framework grains and later cements. With such analyses, predictions of poroperm trends in the subsurface can be made that help both in exploration and production. (J.P.V.L.).

OIL QUALITY

A desire is sometimes expressed for discovering oil of a certain quality, for instance sulphur-free or wax-free oil. Although no wise explorationist wishes to sort his mongrel chickens before they are hatched, a few general conclusions on oil quality have emerged from world-wide discovery experience. Thus calcareous rocks, which often contain some interbedded sulphate as anhydrite or gypsum, tend to produce sulphur-bearing oils with an asphaltic base, whereas sand/shale successions, particularly when deposited in an estuarine environment, tend to produce low-sulphur or sulphur-free oils with a waxy paraffin base. This is illustrated by the difference between Middle East oils, and North African and Nigerian oils. On the other hand, heavy asphaltic oil is sometimes found at the borders of sand/shale basins as in East Venezuela. Geological environments which tend to produce sulphur-rich oil also tend to produce sulphur-rich gas. However, variations in lithology in thick rock successions, the possibility of mixing or changes of composition during migration and variations of source material, make it hazardous to forecast oil quality. Unexpected gas compositions, such as the nitrogen-rich gas in the German offshore and carbon-dioxide-rich gas in many areas, illustrate the

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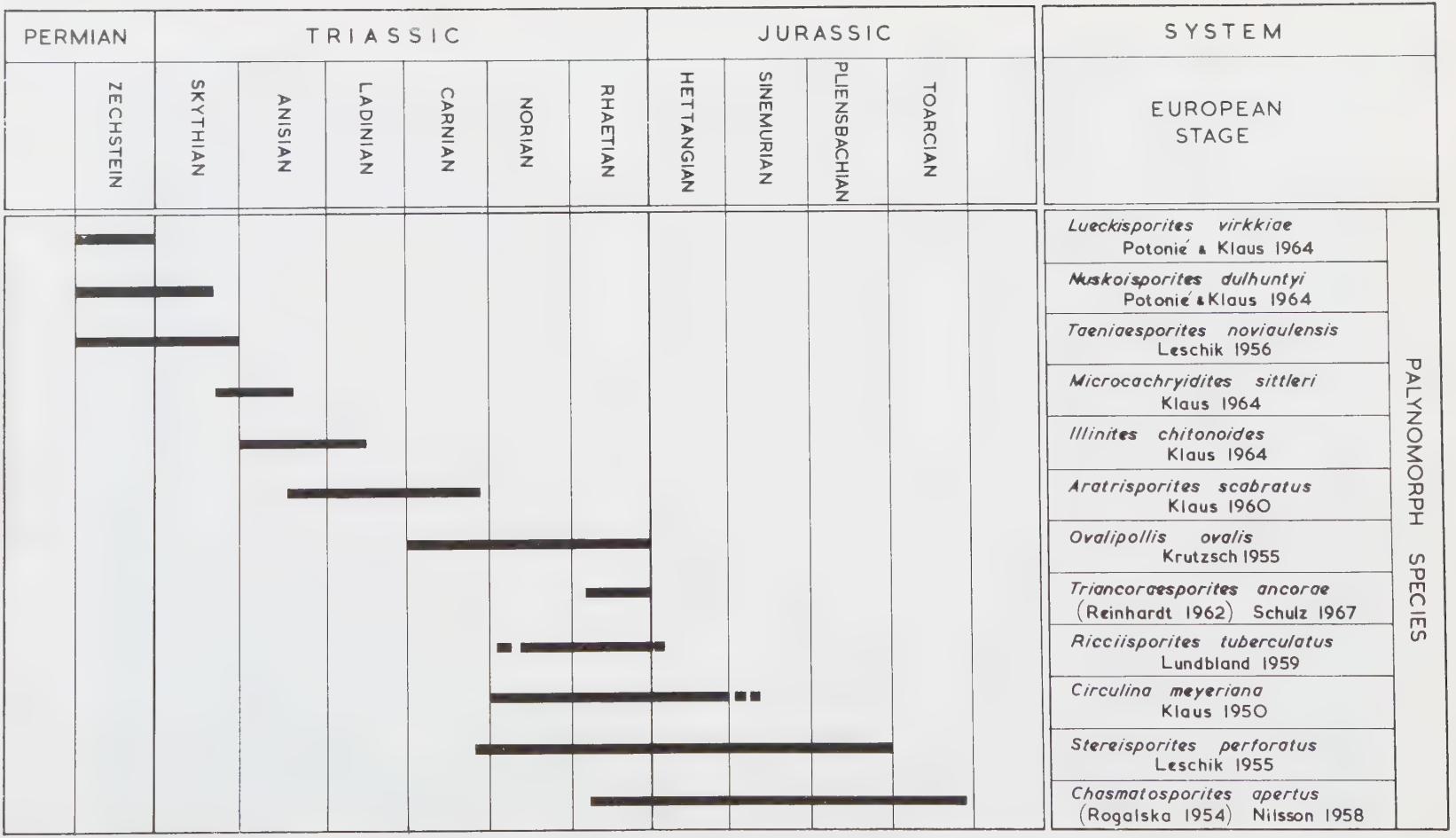


FIG. 2. Palaeontological Range Table. The chart records the stratigraphic ranges of twelve species of fossils (ostracods, foraminifera, spores/pollen) used for correlation and

difficulty of forecasting gas quality: these occurrences can be due to deep geological factors, such as igneous intrusions, which may not be determinable without very deep drilling.

CORRELATION OF STRATA

To investigate rock structure in discontinuous outcrops, or from borehole information, some method of identifying rocks formed at the same approximate geological time must be used. Not many thin rock units of diagnostic appearance extend over very wide areas, such as an ash bed produced by one violent outburst of a large normally quiescent volcano, or a shale rich in the remains of one short-lived, readily identifiable extinct species of micro-organism. There may be considerable doubt whether rocks which are similar chemically and physically are of the same geological age, and this can only be resolved, if at all, by detailed laboratory work. Initially the lithologies of rocks are compared petrographically to see whether the constituent minerals are chemically (composition) and physically (shape) similar. Even if they are, the same lithological types may be repeated during geological time, and a palaeontological study will be essential to reduce the uncertainties. Most species of fossil organisms lived for a considerable span of geological time before becoming extinct. The palaeontologist therefore uses range tables for his correlation work, comparing fossil assemblages rather than individual species for placing rocks in their place in the geological time scale (Fig. 2). Obviously, the more distant the rocks being compared the greater the difficulty of correlation. Correlation between rocks in different basins may not be possible if fossils are not present, or if each basin had its own characteristic fauna, because the mineral constituents of the former land masses which produced the rock detritus from which the sediment was formed may be different.

Palaeontology is a specialized subject world-wide in its scope. It is therefore studied by experts who are generally either macro- or micro-palaeontologists. The work of the latter covers the field of the smaller marine organisms with a wide distribution in former oceans. They are of great importance in oil and gas exploration, particularly in marine exploration where the probability of obtaining identifiable specimens of macro-fossils from the comminuted rock fragments from boreholes is infinitesimal, except when cores are taken (rarely, because of the additional expense).

In recent years palynology, the study of fossil pollen and spores, has become important in correlation. Spores and pollen are distributed by the wind over great distances. They have an almost indestructible covering favouring geological preservation, frequently with a striking ornamentation which may be characteristic for different spans of geological time. They are often identifiable in rocks with no other fossil content. The expert palynologist clearly requires a broad knowledge of past floras and of the many problems introduced by ocean currents and world wind circulations which affect pollen distribution (Fig. 3).

The invention of the electron microscope has provided a valuable correlation tool for use when other methods fail. It has been found that ultra-microscopic plates from the bodies of minute marine organisms have complex shapes characteristic for different geological periods, allowing approximate geological age-dating of very comminuted rock debris (Fig. 4). This is likely to prove very

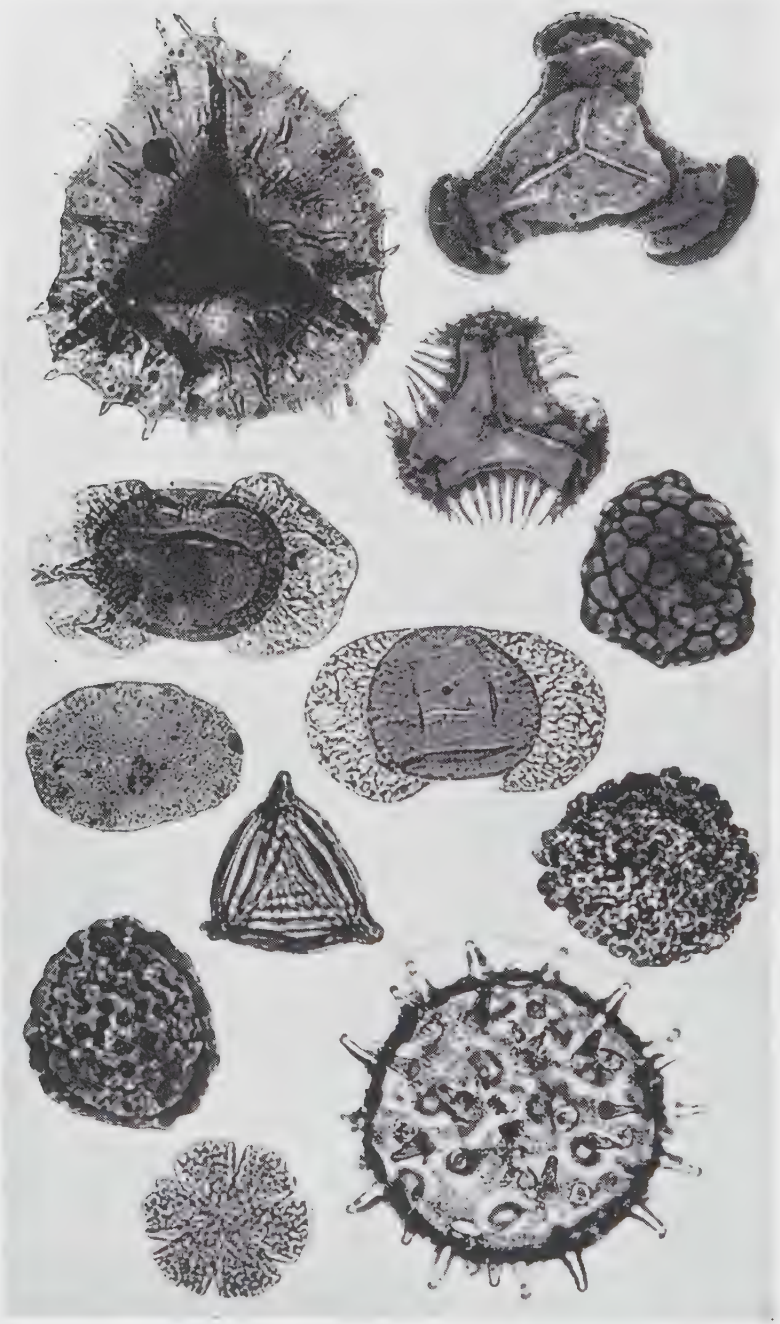


FIG. 3. Fossil spores.

FIG. 4. Fossil coccoliths (Electron micrograph.)

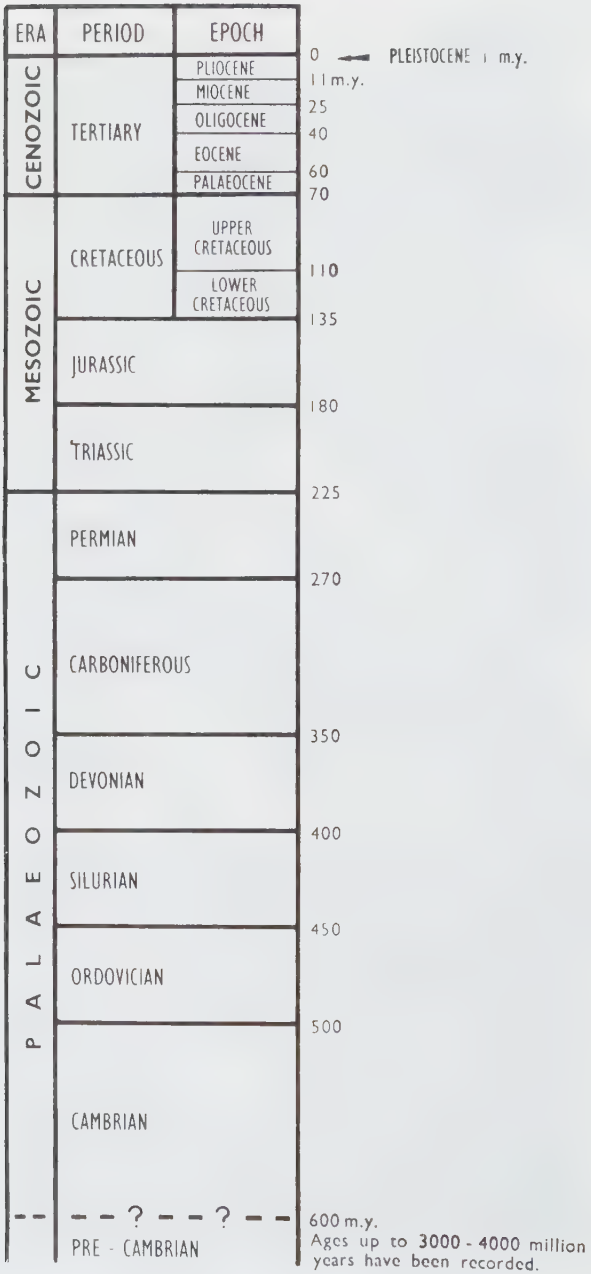


Fig. 5. Geological time scale.

useful as oil and gas exploration advances into the deeper continental shelf waters.

Modern techniques of radiometric age-dating can be of assistance in primary correlation and in working out the geological history of an area on which hydrocarbon migration depends. The radiometric method of age determination is a specialized branch of geochemistry based on estimates of the rate of decay of radioactive minerals. If suitable minerals are present in igneous rocks laid down in sequence with sedimentary rocks, for instance lavas, or in the igneous or metamorphic basement which underlies a sedimentary basin, detailed analysis of the products of radioactive decay entrapped in these materials may allow calculation of the date of crystallization of the mineral in millions of years. As 600 million years of geological time are spanned by the sedimentary rocks in which oil and gas may with justification be sought, the ability to determine that a given rock is, say, about 100 or 500 million years old can be of critical importance in interpreting the geological history of an area on which an exploration programme may depend (Fig. 5).

GEOLOGICAL WELL LOGGING

Obtaining the maximum amount of relevant geological data from boreholes drilled in potentially hydrocarbon-bearing rocks should be a cardinal principle in oil and gas exploration. The rock actually penetrated by the drill at considerable, or great, expense will be an infinitesimal fraction of the bulk of the, as yet largely unknown, rock succession, but the facts provided will form the basis of much future constructive exploration thinking and should be valued accordingly. It is therefore essential for a suitably qualified, alert geologist to be allocated to an exploration borehole, preferably with at least one assistant, to examine and report immediately on all rock cuttings and cores. He

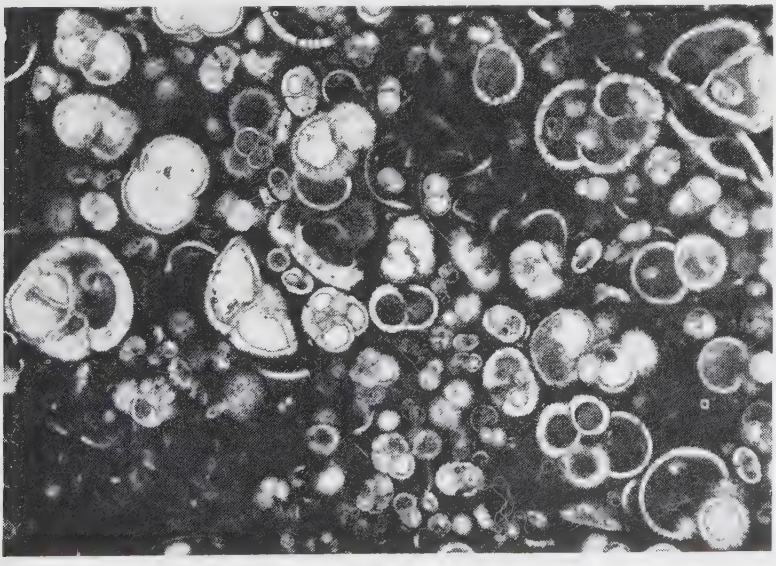


Fig. 6. Thin sections of limestone with micro-fossils.

should be conversant with the exploration thinking leading to the location of the borehole and with the priorities of the various types of information that it will produce. The amount of detailed work required to be done at the well site itself will depend on the type of geological rock succession expected: in limestones thin sections of rock fragments may have to be made for adequate identification, and primary micropalaeontological, petrographical, or chemical examination may be required to allow quick operational decisions to be made (Fig. 6).

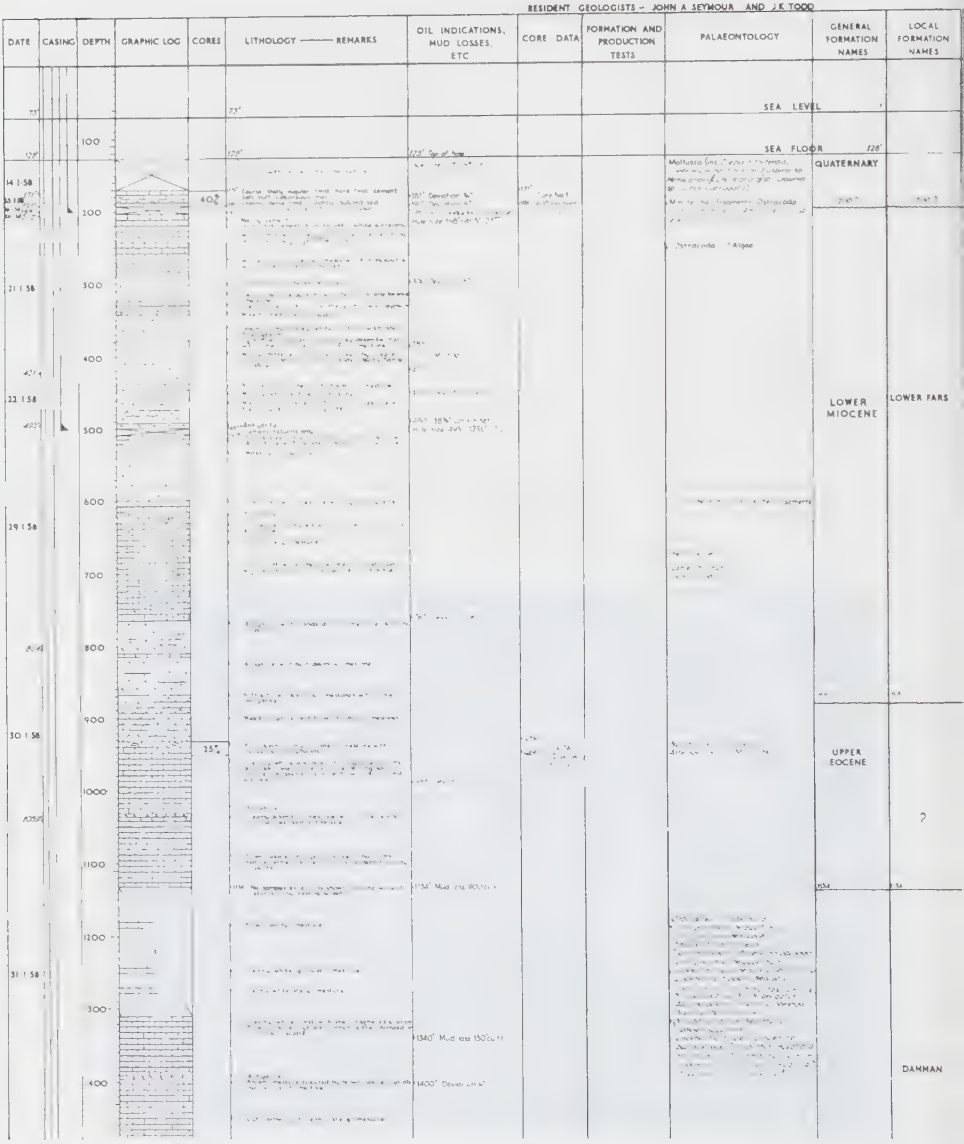


FIG. 7. Part of a geological well log.

The geologist must be skilled in identifying the new rock material in the cuttings which return to the surface and which are screened from the drilling mud and sampled every few feet. Small micro-fossils may pass through the mud screens, and other contamination may occur from rock which has 'caved' (fallen from higher up) from the uncased part of the borehole. He must be very receptive to signs of hydrocarbons at all times. He must work closely with the mud engineer because, for example, mud ringing at the walls of the borehole may occur (when the mud weight is too great) when penetrating porous or fractured strata, and chemical deposits such as salt or sulphates may cause a deterioration of essential mud qualities.

Responsibilities for recording a, perhaps completely new, rock succession in a borehole can be an exhilarating task. It represents the creation of a scientific and commercial asset the inherent value of which will depend on the intelligence with which the work is done. 'Well sitting' should be regarded as an essential stage in the career of all exploration geologists (Fig. 7).

The drilling superintendent and the well site geologist must collaborate closely to reduce to a minimum drilling delays likely to occur if rock examination is left to a central laboratory which has its proper place in confirming and amplifying the work done at the borehole. Identification at the borehole is particularly important when cores are required. Coring programmes agreed in head offices require accurate decisions at the well site to be implemented without expensive delays (although side-wall cores can be shot later to remedy omissions, they give inferior data).

PHYSICAL WELL LOGGING

The amount of geological information obtainable from boreholes has been greatly increased by the development of apparatus which, as it is lowered down the boreholes, can continuously record by electronic means various physical rock parameters. These parameters can be used for the correlation of strata between boreholes; for identifying strata if a cored borehole is available as a standard; for estimating porosity and permeability, hydrocarbon content, water saturation and salinity, and for determining the velocity of sound in the rocks to assist the calculation of depths from seismic records. These tools give logs in graphical form known as electrical, gamma ray, neutron ray or sonic. Further information on this type of well logging will be found in the next chapter.

Physical well logging is a complex specialized technique usually carried out by contractors experienced both in the logging operation and in the interpretation of the results. Within oil company organizations the logging experts are usually in the reservoir engineering departments because the methods are particularly valuable in exploitation work. It is essential that the logging experts and geologists collaborate closely.

Electronic equipment has also been developed which can record the amount and direction of inclination (dip) of the rock strata penetrated by a borehole. This is extremely valuable in exploration as an alternative to the costly process of taking oriented cores. Geological experience is necessary in interpreting dip-meter surveys to exclude local dip anomalies which have no important structural significance.

Physical well logging is not a complete substitute for coring. It is an indirect method of investigating the physical, chemical, and mechanical properties of the rocks, and is much used because it is much quicker and cheaper than coring. Potential reservoir rocks and their immediate cap rocks should ideally be cored in all exploration wells, but usually their depth cannot be accurately forecast in a first hole. It is therefore more practical to drill a first borehole as quickly and cheaply as possible without coring, and then to core in the second hole if the results of the first are sufficiently interesting.

The multiplication of automatic well logging equipment of various sorts has increased rather than decreased the work required of the well-site geologist, and the breadth of the scientific educational background which he needs for the task. Correct interpretation of the indirect evidence which this equipment provides needs judgement based on actual knowledge of the rocks. No machine is infallible, and breakdowns in the absence of an alert geologist can have serious consequences.

It is the responsibility of exploration staff constantly to review their information requirements to ensure that they obtain what is necessary for the solution of their exploration problems. Managers concerned with drilling costs will always follow a conservative policy on these matters and argue for less coring.

FORMATION FLUID PRESSURES AS GEOLOGICAL CLUES

During the drilling phase of the investigation of an area many data which normally lie within the field of the petroleum or reservoir engineer can be of assistance to the exploration geologist. Equivalent pressures in reservoir formation waters can indicate continuity between the rock formation in distant boreholes. If this pressure can be related to outcrop and is in hydrostatic balance with the lowest position of the formation at outcrop, it is reasonably certain that the reservoir is continuous over a wide area. On the other hand, differences of pressures in the same reservoir formation in neighbouring boreholes may indicate a fault or permeability barrier between them, and pressures which are much out of balance with hydrostatic pressure may give important geological clues on structure or stratigraphy.

The chemical characteristics of waters and hydrocarbons can be of value in correlation. Research work has also indicated that the solubility of the aromatic components of crude oil in formation waters may provide an indicator of the direction of an undiscovered oil accumulation if analyses are available from the same reservoir in a number of 'dry' holes: this might have possibilities in areas where the prospects depend on stratigraphy, not structure.

Close collaboration between geologists and petroleum engineers is highly desirable when boreholes are being drilled, to ensure that no useful information is missed. To obtain pressure data and representative water samples is more costly than the running of electric logs because time-consuming packer tests involving special runs of the drill pipe are necessary; the hazards of fishing jobs are also greater.

SEDIMENTOLOGY

Classical geology since the days of William Smith has been concerned with the study of the sedimentary rocks, their mineral constitution and fossil content.

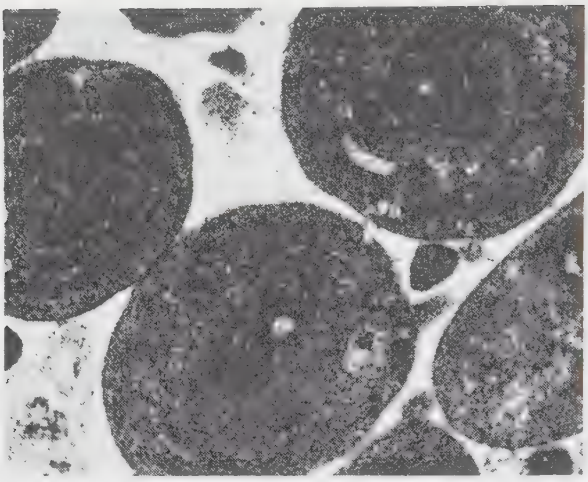
This work was largely devoted to improving correlation and palaeontological dating, and tracing the source of the constituent rock debris. Ideas on the actual mechanics of deposition and the interpretation of the depositional environment from the character of the sediment were handicapped by lack of data from present-day depositional environments, particularly in seas below low-tide level. Stimulated by the development of new electronic recording devices such as the echo-sounder, the sparker or boomer, and the oblique asdic (see p. 67), by the improvement of coring devices and free diving techniques for sampling superficial bottom sediments, the attention of sedimentary geologists has increasingly turned during the last three decades to the collection of data from marine areas. Assisted by this new information, the modern sedimentologist tends to concentrate on the dynamics of sediment deposition. As hydrocarbons originate, migrate, and accumulate within sedimentary rocks, sedimentology is clearly of immense importance in oil and gas exploration. Definite knowledge of past sedimentary environments is difficult to obtain because of the imperfection of the geological record, due to contemporary erosion or later erosion following earth movements, but recent advances in interpretation have been very important. For example, the process whereby coarse detritus can be swept into deep oceanic waters by occasional, short-lived, high-density turbidity currents can now explain the presence of widespread sand bodies in thick successions of otherwise muddy sediments, formerly difficult to understand. And this has brought with it greater consciousness of the very variable amount of time required for the deposition of equivalent thicknesses of different types of sediment. Studies of sediment deposition in the deltas of large rivers such as the Mississippi and Niger in conjunction with data from seismic reflection surveys and hundreds of boreholes have been of considerable value in discovering oil and gasfields in this type of geological environment.

The hydrocarbon-oriented sedimentologist differs from his academic colleague in being keenly interested in the spaces between the solid components of the sedimentary rocks, because these provide the porosity and (depending on the degree of communication between the spaces) the permeability of the rocks on which migration and accumulation of oil and gas depend (Fig. 8). Porosity and permeability are not static. Primary porosity and permeability which existed when the sediment was first consolidated are subject to change throughout geological time: compaction due to the weight of an increasing overburden and mineral crystallization from migrating formation waters can decrease it: chemical changes and solution effects by these same waters or rain water can increase it and produce secondary porosity in localities difficult to forecast. Data on porosity and permeability obtained from surface outcrops may be a poor guide to conditions at depth without the benefit of this type of knowledge.

The history of oil and gas discovery in reef limestones is a good example of the application of sedimentology to oil and gas exploration. As a result of discoveries in Mexico and Canada the data from many boreholes, combined with studies of modern reefs, have been used to build up concepts of reef formation in the geological past which now allow a rational search for similar environments in unexplored areas.

The relatively impervious muddy strata or chemical deposits (such as salt or gypsum) which act as seals or cap rocks and as barriers to the movement of formation waters are of great importance to the oil sedimentologist.

(*a*)



(*b*)

FIG. 8. Thin section of (*a*) porous (*b*) non-porous limestone.

Within the oil industry the sedimentologist has the advantage of numerous borehole records in active exploration areas which may provide complete, or near complete, sections of the rocks being studied. Boreholes may be drilled, cored at critical depths, solely to provide him with critical data. This is in great contrast to surface geological studies which usually depend on discontinuous partial sections, often difficult to join together.

The well-site geologist, if not skilled in interpretative sedimentology, must obtain the assistance of a sedimentology laboratory. It can be of great exploration significance, for example, to know whether a limestone penetrated

by a borehole is a fossil reef, or a sheet of debris derived from a reef, or a fossil offshore bank or a widespread marine deposit: or to know whether a sandstone is an estuarine deposit, a fossil offshore sand bank or a sand likely to be spread over a wide area. An accurate answer to such questions may eventually emerge as more and more boreholes are drilled in the area concerned, but in exploration the great problem is to make an initially correct interpretation when few data are available as this is the time when decisive action must be programmed.

As the amount of sub-surface data accumulates from oil and gas exploration operations it becomes necessary to prepare special types of lithological maps to present the important information in a way which can be easily understood. Examples are isopachyte maps (Fig. 9), which show lines of equal thickness of selected rock formations, and facies maps, which show the areal distribution of the different types of sediment deposited at a given 'moment' of geological time. In much-drilled areas it may become necessary to store borehole sedimentological information on punched cards so that it can be retrieved quickly—or even turned into map form by automatic plotting machines.

As the previous chapter will have shown, the stratigraphic trap in which oil or gas may be accumulated with or without the benefit of structure imposed by earth movement, is of great importance in oil and gas exploration. The

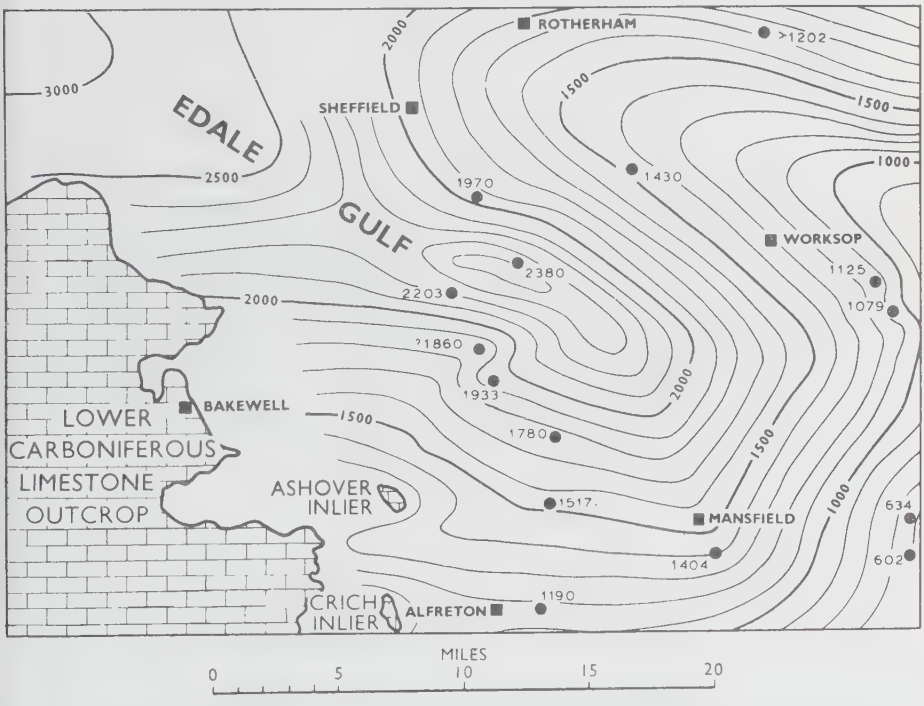


Fig. 9. Isopach map. The figures show the thickness of a rock formation in feet, recorded in boreholes. The contours (lines of equal thickness) have been drawn from seismic data; they show that the greatest thickness of the formation was laid down in the WNW-ESE directed 'Edale-Gulf' of Carboniferous times.

thinking leading towards the search for stratigraphic traps is primarily the task of the sedimentologist. Any forecast of stratigraphic trap conditions in the early stage of an exploration operation must be extremely speculative owing to lack of essential data. As will be explained later, most stratigraphically trapped oil and gas accumulations found so far have either been found by accident in boreholes located for other reasons, or are structural as well as stratigraphic traps (see previous chapter, Table IX). The study of sedimentology must be linked with historical geology and structural geology in the mind of the oil and gas seeker.

EARTH STRUCTURE AND GEOLOGICAL HISTORY

It is necessary to take a broad view of the geology of a region to identify those areas where a downbending of the earth's crust may have occurred throughout a long period of geological time. It is in these areas that great thicknesses of sediments favourable for oil generation occur and from which fold mountains arise. They are usually in the form of oval basins or long troughs, the former tending to occur within the low-lying parts of the present continents and the latter in association with present mountain ranges or past, eroded, mountain ranges. Present geomorphology may bear little relation to the geology of the past, areas of uplift turning into areas of depression and vice versa.

Basin, trough, and mountain formation is part of the large-scale deformation of the earth's crust due to thermal activity in the earth's interior where convection currents are thought to keep the molten or plastic rock material in gradual slow motion. The more solid outer crust adapts itself to the stresses so produced, and this is the cause of the earth movements studied in structural geology.

Some basins have retained a simple form following downbending and sediment infilling; others have had a more complex form imposed on them by folding or faulting, often during sedimentation. Hundreds of thousands of boreholes in basins all over the world tell us that oil or gas tends to occur in any type of structural uplift which may be present within a basin or on its flanks. It is an important task of petroleum geologists to work out the geological history of basins, mapping the changes of type and thickness of the sediments which occur within them and the structural changes which have affected them, so that concepts can be formed of the probable times and patterns of oil and gas movement. The concepts of plate tectonics, continental collision, and subduction are useful paradigms in regional geological thinking, but they do not change the criteria required for oil and gas discovery.

The characteristic of most mountain ranges is that they are linear features which arise from long troughs which become filled by thick sediments (commonly as much as 30 000 to 40 000 ft). In the course of geological time a wave of compression usually passed across these troughs, causing a line of uplift to form one one side and a new depression on the other side. The detritus from the erosion of the uplift then begins to accumulate as sediments again in the new depression. These waves of crustal movement may follow each other in phases of several million years. On the uplifted side of the trough compressional folding tends to occur. On the other side of the trough, where the infill of sediments thins out against the edge of the trough, the structures will be more

gentle and stratigraphic traps may occur. Oil and gas may accumulate in any suitable traps wherever the sediments have been suitable for oil generation within these basins.

The presence of rifting in older rocks below a sedimentary basin, or below a gentle uplift, due to former extensional crustal movements must always be borne in mind ('pull-apart tectonics'); this is well illustrated by present knowledge of the North Sea basin. Structures favourable to oil accumulation may also be associated with lateral movement between crustal blocks, but there is the risk of fractured cover rocks in such areas.

A useful method of summarizing available information about the geological past is by the preparation of palaeogeographical sketch maps showing the distribution of land and sea as it is thought to have been at some convenient geological time. Figure 10 shows the general distribution of land and sea in the North Sea area in Permian times when the saline rocks of the cap rock formations were being formed which prevented gas escape from the basal Permian reservoir sandstones below them, the gas having formed in the

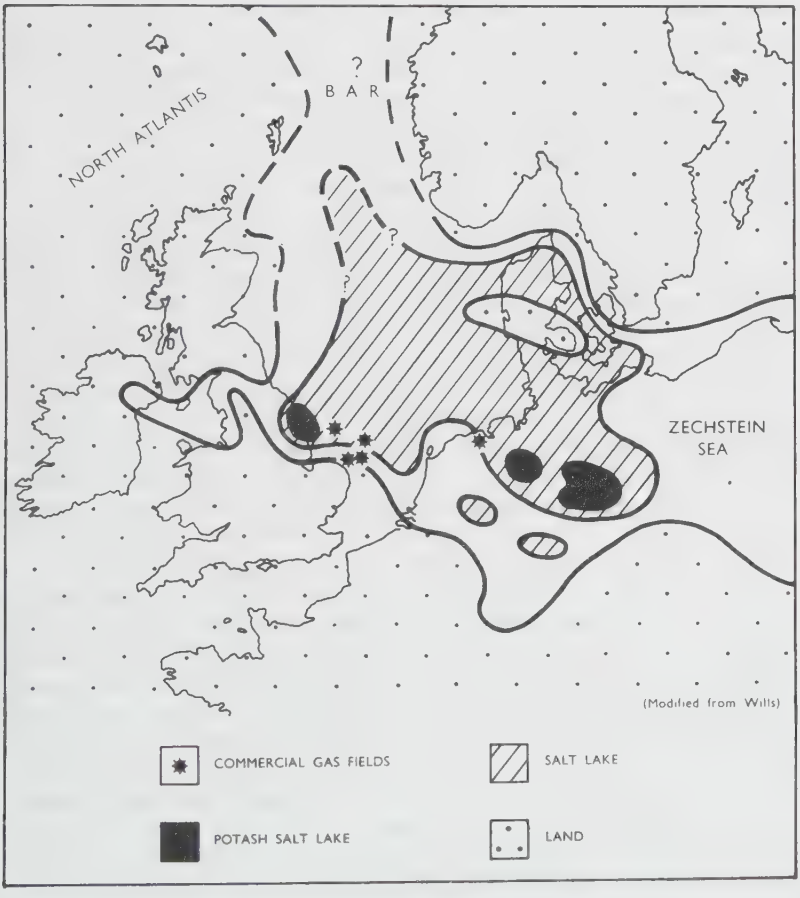


Fig. 10. Palaeogeographic map of North Sea in Permian times.

underlying coal measures. Such graphic representations of working hypotheses must be used with caution, particularly by laymen or non-specialists; they change their shape frequently as new information comes in from boreholes.

Although oil and gas may be found simply by drilling on structure, paying very little heed to geological history, this is a very short-sighted method of exploration. Success goes in the long run to those who have accumulated as much information as possible about the geological histories of prospective areas. Only by this means can the probable past pattern of hydrocarbon movement in the various formations be inferred and the best decisions be made for operational programmes.

GEOLOGICAL TIME AND MIGRATION

Geological time is so vast in comparison with the life of man that it is not easy, even for the geologist, to think geologically with a proportional time sense. Research on historical geology has been assisted in recent years by the development of radiometric methods of dating the time of formation of rocks in millions of years (referred to above), a possible technique which was first thought of by Rutherford in 1906. The age of many minerals, and the rocks in which they occur, can now be determined within limits which are relatively narrow when expressed as a percentage of geological time since their crystallization. A geological time scale from data published in 1959 is reproduced in Fig. 5. The oldest sedimentary rocks of economic interest to the petroleum geologist were formed 600 million years ago, with a margin of error of between 3 and 4 per cent. It will be seen from this diagram that the length of the named geological periods in general use by geologists is very variable. The Cambrian period, for example, is longer than the whole Tertiary era and about the same length as the combined Silurian and Devonian periods. The major paroxysms of mountain building appear to have occupied relatively short periods of geological time. The Himalayas, formed since the Miocene period ended about 10 million years ago, on good morphological evidence were probably uplifted to their present great height during the last few million years, a rate of uplift of a few centimetres a year, insignificant to man but in geological terms very rapid. Recent estimates of other slow crustal movements, including major subsidences and lateral continental drifting, are also in the range of a few centimetres a year.

But very sudden crustal movements are well known to man; differential movements of a number of metres along fault lines in earthquakes may take only a few catastrophic seconds. It is clear that an average rate means very little in geology. A thick rock succession may include vast periods of non-deposition of sediment; coarse beds such as sandstones may be deposited in a geological instant, in a few weeks or days on the human scale, whereas muds in quieter conditions may accumulate in millimetres a year, taking tens of thousands of times as long to grow to an equivalent thickness. Time considerations such as these must be given some weight in assessing the potentialities of a hydrocarbon prospect when sufficient geological data are available—that is usually some time after the start of exploration operations. In general the longer the period of geological time available for the accumulation of the prospective sediments and the migration of water, oil, and gas within them the better, particularly if

the structures in which the hydrocarbons may accumulate are large. Once a cap rock has been deposited it is less important whether the structures themselves are formed relatively quickly or slowly, except in so far as rapid folding increases the probability of vertical migration due to fracturing and to loss by seepage unless a first class cap rock is available. The oldest part of the composite oil in the Asmari reservoirs of South-West Iran probably began its history of formation and movement in the Jurassic about 150 million years ago, but accumulation in the Asmari Limestone reservoir below its evaporite cap rock started only about 15 million years ago. On the other hand, the whole process of sediment deposition and oil accumulation in the Niger delta area has taken place within the last 15 million years, but here the accumulations in sandstone reservoirs are much smaller.

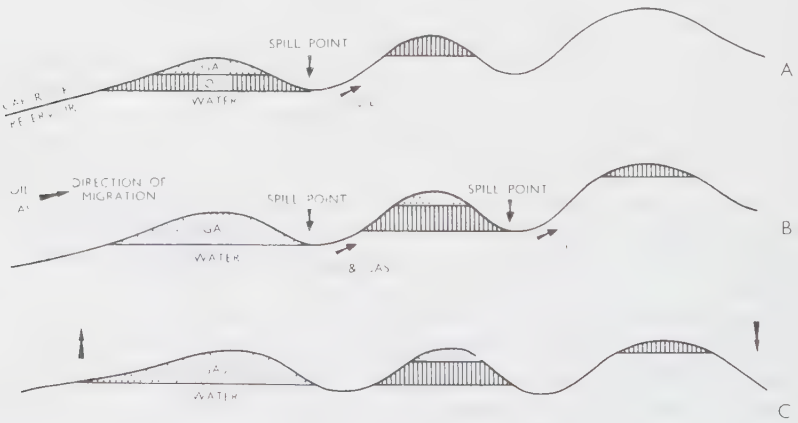
Only very slow fluid movements in permeable strata are required in the abundance of geological time to achieve all that our observations tell us must have happened. One millimetre of movement a year is 1 km in a million years; 1 cm a year would be time enough for the accumulation of the Asmari Limestone oilfields, if it is assumed that none of the component oils moved more than about 100 km from their source rocks and 10 million years was required for the accumulation.

But the recent example of a rapid migration of gas from a deep Jurassic reservoir below the Lower Miocene Asmari Limestone reservoir in the Masjid-i-Sulaiman field, via faulty well casing, into a subsidiary reservoir in the Eocene, and from thence into the Asmari Limestone itself, shows that fluid movements rapid in human time can occur. Similar events, which would be catastrophic in geological time, must occur when thick rock successions susceptible to fracturing are strongly folded or faulted. It has been suggested that much of the oil in the Asmari Limestone came into its present position very rapidly at a very late stage in folding when fracture connection was established with the underlying Mesozoic reservoirs. This is more likely to happen in carbonate provinces than where sandstones and shales formed a significant part of the succession.

The movement, or migration, of oil and gas from the source rocks, where they are thought to have been formed, into the reservoir rocks where it is hoped they may have been concentrated in the various types of trap, is the background thinking of all oil and gas exploration. The energy causing this fluid movement is mostly gravity, although earth compression and capillarity play a part. The difference in their specific gravities separates the gas, oil, and water below the cap rock. The process of concentration takes place very slowly in geological time and is influenced by all the earth movements suffered by the rocks since the oil began to form. In horizontal strata only the forces due to compaction and capillarity influence fluid movement into the porous rocks. But if the strata become tilted differences of pressure occur, and fluid movement will take place from localities with higher pressure to those of lower pressure. It is the task of the exploration geologist to use his imagination and try to visualize the probable geological history of a prospective area as a changing pattern of fluid movement. As very few, or no data are usually available at the start of an exploration campaign, at this stage all the thinking tends to be purely speculative and to be based on analogy with other areas where exploration is more advanced.

It is clearly of some importance that the desired structural traps should be formed as early as possible, preferably before the oil and gas make their primary movement away from the source area. Many barren structures were formed too late for accumulations to be formed in them. A major reversal of dip, however, such as may be caused by the uplift of a basin or trough of deposition, may cause oil and gas to make a secondary migration back towards the original source area, and originally barren structures may thereby become charged. The more restless the structural history of an area the greater the possibilities for secondary or even tertiary migration and ultimately of oil loss. This will increase the chances for all structures accumulating some oil or gas, by redistribution, but will reduce the chances of any major accumulations surviving. W. C. Gussow has done a service to exploration by his clear enunciation of the theory of differential entrapment which, originating in the Middle East, explains how, under ideal lithological and structural circumstances with widespread permeable reservoir rocks, oil and gas can become separated during up-dip regional migration through a series of structural traps (Fig. 11). Although continuously permeable reservoirs of great extent are very rare, the theory of differential entrapment is a useful stimulus to exploration thinking, particularly when information from boreholes becomes available. It can provide a serviceable explanation for the separation and grouping of oil and gasfields in certain types of basin and fold systems.

An important stimulus to secondary migration of oil and gas can be provided by erosion which, by reducing the hydrostatic head due to the elevation of the reservoir formation at outcrop, changes the pressure regime down-dip. Speculative visualization of the whole concentration process throughout geological time usually pays good dividends, particularly when an exploration operation is well advanced and the data from a number of boreholes are available. It is clear now, looking at the discoveries to date, that those



DIFFERENTIAL ENTRAPMENT THEORY

Fig. 11. Differential entrapment. In A and B oil and gas are shown moving from left to right up the regional dip. In C regional tilting (down to the right, up to the left) has stopped migration.

companies which correctly visualized the most probable area of good sand development on the south-west flanks of the basin with good migration possibilities made the largest gas discoveries in the North Sea; they had a reasonable amount of data from the Dutch land area on which to base their speculations.

The discovery of a major oilfield on the Arctic slope of Alaska was an example of oil and gas discovery due to action based on speculative hypothesizing about migration and reservoir possibilities. Most of the area was for many years a Petroleum Reserve of the United States Navy. An exploration campaign carried out for the Navy at the end of the Second World War proved the area to be hydrocarbon-bearing in several boreholes, some near the north coast, but nothing large enough for export was found. Some years later part of the Arctic Slope was released for leasing and normal competitive operations began. A number of major oil companies did geological work, carried out geophysical surveys, and drilled boreholes on structures in the foothills of the Brooks Range where, on analogy with other areas, prospects seemed the best. But after considerable expenditure in an inhospitable region, where geological, gravity, and air survey work could be done in the short summer but seismic work and drilling were only practicable in the winter, no discoveries were made, largely because of a shortage of reservoirs. Some operators withdrew. Others turned to the coastal area following different speculative ideas. Gravity and seismic surveys revealed a major coastal high where good reservoir conditions seemed possible. The new working hypothesis proved successful; perhaps, it may in due course be shown, for the wrong reasons, for truth usually emerges slowly in geological work.

STRATIGRAPHIC AND COMBINATION TRAPS

An oilfield or a gasfield in a reservoir sealed by a permeability barrier which may have been tilted by earth movement, but has not been folded or faulted in such a way that this has affected the accumulation process, is called a stratigraphic trap because the accumulation has been due to stratigraphic factors. An isolated sand body, for example an offshore sand bar completely surrounded by muddy sediments, may contain a stratigraphic accumulation if hydrocarbons have entered it from these muddy sediments and are unable to migrate further (Chapter 1, Fig. 4). A coral reef can form a stratigraphic trap if it is surrounded by muddy sediments and sealed by a cover of impermeable muddy or chemical sediments. Many dispositions of porous sedimentary rocks within impermeable strata capable of providing stratigraphically trapped oil or gas can be visualized by the petroleum geologist by analogy with actual discoveries which have been made. This is particularly the field of study of the sedimentologist, and becomes increasingly important as subsurface data accumulate in an active exploration area. While it is often possible to indicate in general terms those parts of a basin or trough where stratigraphic traps might occur it is usually extremely difficult to locate them with sufficient accuracy for test drilling. Modern reflection surveys can indicate convergences of strata which provide a suitable geometry for stratigraphic trapping, but they cannot give reliable data on the essential sedimentological factors of porosity and impermeability on which accumulation, and survival of an accumulation,

depend. The presumed target can only therefore be investigated by trial-and-error drilling. If a first borehole finds a good impermeable formation at a convergence, a second borehole is necessary further down-dip to see whether a reservoir is present. If a reservoir containing saline water is provided by this second borehole, conditions for stratigraphic trapping have been partially proved, although there are still no data whatever about the permeability barriers which are necessary on the flanks for the hoped-for accumulation. Several more boreholes may be required between the first two holes to discover or to disprove an accumulation. Such trial-and-error drilling is inevitable in all stratigraphic test prospects, which are consequently greatly inhibited by drilling costs. Geochemical data can assist the search for stratigraphic accumulations.

Most stratigraphically trapped oil and gas have been found by accident, or in boreholes located on structural evidence, rather than by deliberate programmes. In very petroliferous sand and shale prospects, such as Lake Maracaibo and the Mississippi delta, stratigraphic test exploration programmes may be economically justifiable, but even in such areas most test wells are located on subsurface structural contour maps, constructed from borehole evidence and seismic data which have to be continually amended as more evidence becomes available.

A stratigraphically trapped oil or gas accumulation formed early in the history of a basin may subsequently be folded or faulted by earth movements in such a way that the oil or gas will be further concentrated in any structural highs so formed, increasing the height of the oil or gas column, but decreasing the area of the accumulation, unless the earth movements stimulate a renewal of oil and gas migration from the source sediment area. It is usually difficult to prove that oil and gas found in structural traps were not originally stratigraphically trapped, because the evidence is likely to be found in the structurally low areas normally not tested by boreholes. But, if it is conceded that some oil or gas is generated early in the history of a sedimentary basin, this material must either stay where it is formed or migrate somewhere else during the interval between formation of hydrocarbon and structure. This may amount to millions of years. During this long time the slow sinking of a basin must produce some inclination of the rocks formed in it. And the expression of the formation waters from the sediments as they are compacted by the weight of their increasing overburden must produce some water movement. Some migration of early-formed hydrocarbons seems inevitable therefore. This will be assisted by the differing densities and surface tensions of oil, gas, and water. Stratigraphic trapping will then tend to take place at any barriers which can contain the small forces involved. While barriers may be entirely stratigraphic it is more probable that during the course of geological time some degree of differential movement will have taken place in the underlying basement, producing faulting or flexuring, making it likely that some structural barriers will be present as well. It is therefore probable that even early accumulations of oil and gas will be against barriers to fluid migration which are partly stratigraphical and partly structural in origin: these have been termed combination traps.

The uncertainties introduced by combination traps are illustrated by a case from north-west Germany, where an initial borehole was drilled on what

appeared at the time to be close to the highest point of an anticline half delineated during the course of a seismic reflection survey. It discovered an important oilfield in a sandstone reservoir. Later, when the seismic reflection survey had been completed, it was found that the successful location was some way down the axial plunge of the anticline. Another borehole was drilled in the true crestal position. No reservoir was found, only shale. Had the crestal well been drilled first in the best structural position the oilfield would have been missed because accumulation was in a combination trap at one end of the anticline only. No structure can be adequately tested by only one borehole if stratigraphical conditions allow a possibility of permeability barriers being present. It can be argued that, unless the distribution of the reservoir formations is so well understood that facies maps can be drawn, at least four test wells are necessary for a complete investigation of one anticline or dome.

Another factor favouring combination traps is that differential movements of the basement during sediment deposition will tend to favour the production of reservoir formations above basement highs where current energy on the sea bed is likely to be higher, sweeping the finer-grained sediment into lower positions.

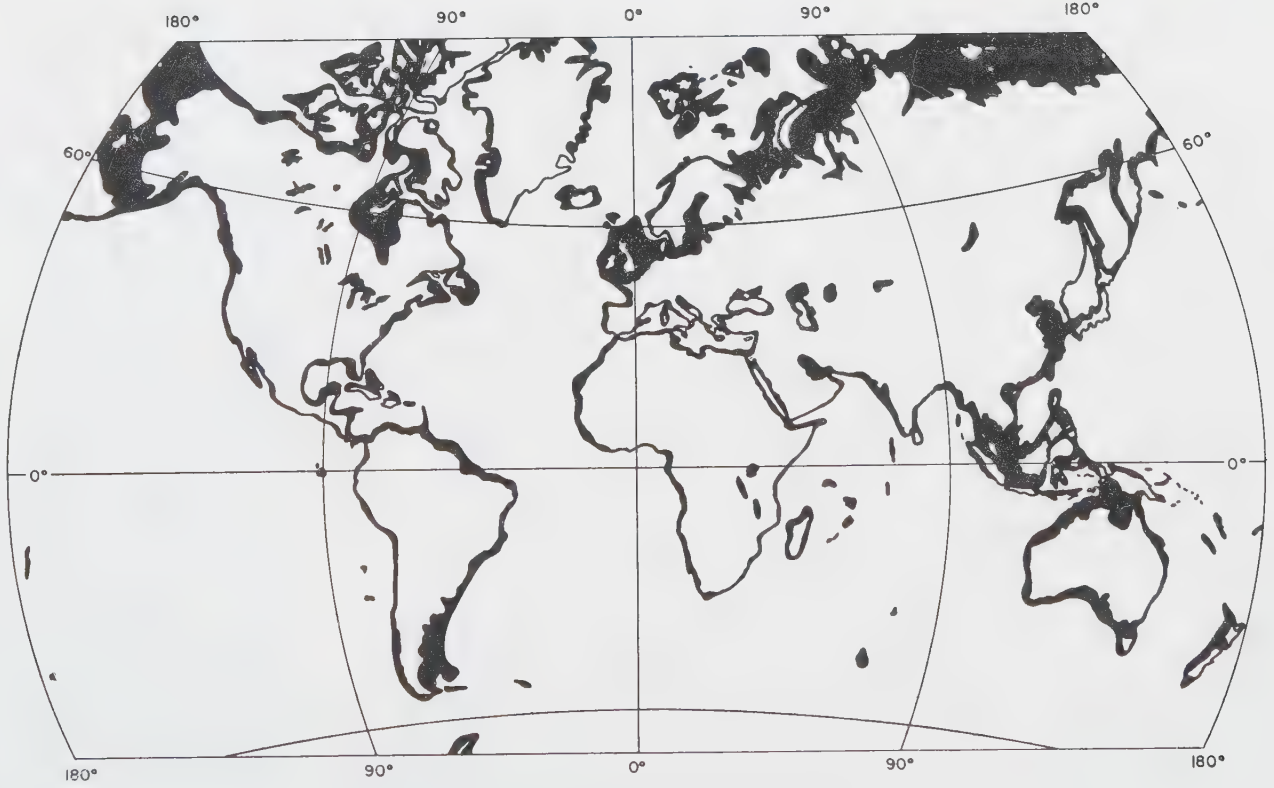
For practical reasons, even where stratigraphically trapped accumulations can be visualized, test wells will always be located initially on structural highs even if the reversal of dip is very slight. Such locations can conveniently be termed combination tests to show that stratigraphic reasoning has played a part in their selection.

For many years exploration promoters have extolled the stratigraphic trap as the great incentive for further exploration when the structural targets have been exhausted. But, for the economic reasons already explained, it has so far been found preferable to look for new structural targets in less explored or entirely new areas, such as continental shelves, instead of re-examining old prospects for stratigraphical accumulations. Under the competitive system of exploration enterprise this process is likely to continue, except where governments take economic actions having a drastic effect on local exploration costs, amounting to subsidy, or until a real shortage of world structural targets makes itself felt.

CONTINENTAL SHELVES

The earth's crust is now known to be divided into two types, continental and oceanic, below which lie the vastly more bulky and heavier mantle and core. The continental crust, which is three to four times as thick as the oceanic crust, includes all the major land masses which have submerged borders. These submerged outer borders are called the continental shelves. They extend beyond the present continental shores to an average depth of about 75 fathoms or 135 metres. From the edge of the continental shelf the surface of the continental crust slopes down gradually towards the deep oceanic basins which are underlain by the thinner oceanic-type crust. The thickness of the continental crust decreases gradually below the continental slope until the thinner oceanic crust is reached.

Under the 1958 Geneva Convention, ratified in 1964, it has been internationally agreed that the continental shelf shall be legally defined 'as the



WORLD CONTINENTAL SHELVES

FIG. 12. Continental shelves, including major inland seas and lakes, and some marine platforms within the 200 m depth range.

sea bed and subsoil of the submarine areas adjacent but outside the area of the territorial sea to a depth of 200 metres or, beyond that limit, to where the depth of the superjacent waters admits the exploitation of the natural resources of such areas' (Fig. 12).

The top of the continental slope has no particular significance in local geology and oil and gas prospectiveness may extend beyond this down the continental slope. Drilling and potential exploration costs have so far prevented commercial investigation of the continental slope for oil and gas accumulations, there being no reason to expect the prospectiveness of the outer part of the continents to be better than on the continental shelf, the contrary being more probable.

As they form part of the continents, with the same general type of geological structure and composition, the continental shelves must be subject to the same sort of exploration thinking as the land areas. Search must be made for basins and troughs with thick sediments in which there may be adequate structural traps. It is clear that to achieve economic discovery in the marine environment, with all its extra costs and hazards, conditions for oil and gas accumulation must be considerably better than the average onshore prospect to be attractive to the realistic operator. An obvious disadvantage of the shelves is that deposition of prospective sediment is likely to have come from one side only, which reduces its bulk potential, except where large masses of sediments brought down by past or present major rivers have been accumulated in relatively restricted areas, such as the Mississippi and Niger deltas. Excluding such delta prospects the most important water-covered oil and gas provinces found so far are really within the continents, rather than true shelves, for example the Persian Gulf, Lake Maracaibo, the North Sea and even the Bass Strait. A corollary of the one-sidedness of the true shelf areas is that factual geological knowledge is usually extremely one-sided—very little is known about the rocks or rock structure in most areas of the outer shelf, and practically nothing below the continental slopes. It is obvious therefore that estimates for the potential oil and gas reserves of the continental shelves must be very subjective, particularly if made by statistical reasoning, which in geology can be very misleading because of the importance of anomalies.

The continental shelves of the world are receiving great attention at the present time. The exploration tool par excellence is seismic reflection survey which is more rapid, more efficient, and generally gives better results than on land and is often less costly on a line-mile basis. As explained elsewhere, gravity surveys are little used in marine areas, but aeromagnetic surveys are very useful in the reconnaissance phase. Marine exploration can only proceed satisfactorily by locating boreholes on structural contour maps made from the results of seismic reflection surveys, drilling boreholes, studying the sedimentary succession obtained and then revising the contour maps on the basis of the geological data obtained, if necessary after further seismic surveys, should the rock succession justify this.

THE DEEP OFFSHORE

Hollis D. Hedberg, in a paper entitled 'Why Explore the Deep Offshore?', has summarized the geological reasons which make it advisable for the oil industry

to take some interest in the continental slopes and deep ocean basins. This has been accentuated by the recovery of cores with oil indications in the Sigsbee Deep, Gulf of Mexico, in water 12 000 ft in depth. Exploration in the deep offshore has so far mostly been done by oceanographic institutions, universities, and government agencies, but with the increasing demand for oil and gas it would be logical for industry to participate in the interests of the long-term supply situation.

SHALLOW DRILLING FOR STRUCTURE

If an area of exploration interest is entirely covered by a thin veneer of recent sediments, such as alluvium, shallow information boreholes may be a useful first investigation before geophysical surveys. This will usually depend on the economics of access and the type of rocks expected below, particularly their hardness. In a well-developed country there is no technical difficulty in drilling some hundreds of feet with a small rig mounted on a suitable vehicle. The value of the boreholes will depend on the ability of the resident geologist concerned to correlate the strata encountered in the various holes, and this will be greatly assisted if portable electric logging equipment is available. The location of successive boreholes can then be decided as the subsurface data become known, a great advantage. As gradual processes of uplift which form structural highs in the course of geological time may be interspersed by periods of erosion, or by regional tilting, it is rarely safe to infer that deep structure will conform exactly to shallow structure, so a shallow drilling programme will probably have to be followed by seismic work before deep boreholes can be located safely.

In less-developed countries the logistics of shallow drilling programmes are less favourable, and it will usually be more economic to proceed direct to seismic reconnaissance for structural information, even at shallow depths, using the seismic shot hole rigs for obtaining near-surface geological data in critical places as necessary.

Shallow drilling gave much useful geological information in the north-west German plains area where the rocks are concealed by a thick superficial accumulation of glacial and alluvial deposits. The southern North Sea area would doubtless have been investigated initially in the same way had man reached the technological age 10 000 years earlier.

It is possible to drill and core to about 1000 ft with a modern vehicle-mounted rig of lorry type and to drill to a hundred feet or more with a rig mounted on a Land Rover. In shallow seas coring is practicable to several hundred feet from specially equipped small craft.

DEEP DRILLING FOR STRUCTURE

It is, of course, possible to investigate deep structure by the drill as well as by seismic surveys. This has the great advantage of providing stratigraphic as well as structural information. But economics usually decides against this. The cost of drilling increases greatly with depth and also the time necessary for completion, particularly if there is any real risk of striking hydrocarbons accidentally. Moreover, unless the concealed geology is expected to be structurally simple and relatively free from faulting, it is not possible to ensure

that the boreholes are located in the most favourable places for obtaining the information required without preliminary seismic reconnaissance. Deep structure drilling, therefore, is usually required after a seismic survey when some important seismic feature, such as a line of poor reflections, introduces difficulties of interpretation. The value of such holes, however, usually depends more on the stratigraphic information obtained than on direct structural data, unless a borehole dip-meter device can be used for measuring the inclination and direction of inclination of the strata, or several boreholes are drilled.

STRATIGRAPHIC TESTS

A borehole drilled essentially for stratigraphic information and not located to investigate structure is usually called a stratigraphic test. The term is not entirely satisfactory because structural drilling depends on stratigraphic correlation, and no stratigraphic test can fail to give some structural information. Moreover, all initial test wells located on deep seismic structure provide entirely new stratigraphic information in areas where the subsurface geology is unknown.

In the history of oil and gas exploration a number of cases are known where, exercising hindsight, it is possible to say that had an early deep test been drilled purely for stratigraphic information it would have saved years of work and expedited commercial discovery. Early managements tended to dismiss proposals for such wells as 'pure geological curiosity' without appreciating the possible dividends. Thus in the late 1920s false geological ideas were current on the likely stratigraphic column below the north-east coast of Arabia. One deep borehole located anywhere in this area would have revolutionized geological thinking and changed the pattern of future operations, advancing oil discovery by a number of years. In the late 1930s curiosity was expressed by the original geological survey party about the unknown rock succession under the Niger delta area. Had this curiosity inspired an early deep borehole the nature of the delta prospect would have been appreciated quickly. But years of classical type geology on the outcrops and of seismic surveys in areas adjacent to outcrops supervened, and a number of unsuccessful test wells were drilled, before the operators investigated the younger delta sediments which proved to be so rich in oil and gas. There must always be a case for considering the economics of an initial deep stratigraphic test in any area where the presence of a thick column of sedimentary rocks is inferred but their nature is not known: knowledge of this stratigraphic column and its seismic properties can be of great assistance in planning subsequent seismic surveys, interpreting geophysical data already obtained and evaluating the prospect on sedimentological grounds.

One of the advantages of the competitive method of exploration is that boreholes drilled by other operators, from which the geological information can often be obtained by exchange or purchase, provide valuable information at relatively small cost. And not infrequently competitors will drill a joint stratigraphic hole to their mutual benefit.

APPRAISAL AND DEEP TEST DRILLING

The discovery of an oil or gas accumulation does not mean the end of exploration. A new field must be appraised by step-out drilling, with or without

detailed seismic surveys to assist location. Appraisal is local exploration. In simple structures the nature of an accumulation may be learned relatively quickly and the appraisal stage may be short. But sooner or later there will be a demand for another exploration borehole to drill to a greater depth unless strata which denote the end of prospectiveness have already been encountered. Sometimes greater regional knowledge or improved seismic interpretation may suggest that an unconformity or even low-angle faulting may be present at depth and another, more costly exploration campaign may be justified.

TOPOGRAPHIC SURVEYING

A topographic mapping service is essential in all exploration survey work to record accurately or to assist other exploration staff to record the position of observation stations and obtain levels to the appropriate degree of accuracy. The services required will vary from high-grade geodetic triangulation to approximate fixes for reconnaissance surveys, depending on the stage of development of the country being explored. It is greatly to the advantage of an exploration organization to have its own survey department with surveyors experienced in the type of work required. In undeveloped countries photogrammetric methods of primary and detailed survey are much used: much of this work is done by contractors who are specialists. In the last three decades electronic navigation methods have become essential for offshore exploration where it is necessary to determine the position of a ship quickly and accurately. In the North Sea special Decca chains have been set up and satisfactory fixes are obtainable. A section on position fixing for geophysical surveys will be found in the next chapter.

In undeveloped countries or marine prospects where accurate topographic control points may be lacking, it is advisable for competing exploration organizations to collaborate on survey methods to avoid the chaos of a number of uncoordinated surveys of varying accuracy. When concessions are allocated on the chequerboard block system it is usual for the government concerned to specify the degree of accuracy required because legal boundaries are involved. The use of satellites in position-fixing at sea has greatly assisted marine exploration operations during the past decade.

GEOPHYSICAL METHODS

The three geophysical methods of greatest use in oil and gas exploration are gravity, magnetic, and seismic, the last including the refraction and reflection techniques. These form the subject of the next chapter and will only be discussed here from the geological viewpoint. The gravity and magnetic methods are used only in primary surveys where little is known of the geology at depth and where it is desired to ascertain whether a sufficient thickness of sediments of potential prospective interest is present. It is the seismic reflection method which is now universally used for determining underground geological structure on which boreholes have to be located.

Magnetic

The strength of the earth's magnetic field as recorded at the earth's surface is mostly due to the magnetism of the material below the crust and of the older rocks within the crust. Sedimentary rocks are usually poorly magnetic and contribute little to the magnetic picture. Magnetic features have less effect when they are further away from the measuring instrument; therefore the picture obtained over a deep sedimentary basin usually has smooth contours. The development of the airborne magnetometer has made it possible to fly aeromagnetic surveys over land areas difficult to survey on the ground, and over marine areas, along carefully spaced flight lines. This is a relatively inexpensive and rapid method of primary survey, appropriate for looking for unknown major depositional basins on land or the continental shelf. Owing to the magnetic effects which can be caused by bodies of basic igneous rocks, the interpretation of magnetic maps in shallow sedimentary basins in terms of sediment thickness is hazardous. It is not advisable to use the magnetic method for locating individual structures for test drilling, except when considerable subsurface geological knowledge is available.

Gravity

The earth's gravitational field as recorded in a small area is considerably affected by variations in the density of the near-surface rocks. In areas with poor outcrops, where the underlying rocks have been folded or faulted and then truncated by erosion, gravity highs often coincide with anticlines or fault block highs, because in general the older rocks they bring closer to the surface tend to be denser than younger rocks. Gravity lows tend to coincide with synclines or downfaulted blocks. Owing to the varying densities of the different types of sedimentary rocks, however, interpretations cannot be unique and gravity features are used only as guides for subsequent seismic investigation, not for borehole location. Exceptionally, boreholes may be drilled for stratigraphic information on gravity features when these can be interpreted with some confidence as, for example, the marked lows due to thick accumulations of low-density salt in salt plugs.

As with magnetic surveys, gravity surveys can be of great assistance in locating the deep basins of thick sediments which are the primary targets in oil and gas exploration. For gravity surveying the ground should preferably be reasonably flat, otherwise difficult corrections have to be made for height differences. In marine areas gravity surveys are less used because of the greater difficulty of making the observations, and the need to employ a ship, which is more productive when surveying seismic reflection lines.

Seismic Refraction

The seismic refraction method was originally developed to locate the concealed masses of salt forming salt plugs (in Germany), and later to trace major anticlinal axes in massive limestones (in Iran) which could not be located from surface geology. In both cases the success of the method depends on the fact that

the shock waves caused by the explosives used for the surveys travel faster through the salt and limestone than through the rocks associated with them. The method is now little used for delineating structure, except in areas where for some reason the reflection methods fails to give results. It is, however, still a useful reconnaissance tool for determining the depth to high-velocity metamorphic or igneous basement below a little-known sedimentary basin, or for investigating the possible presence at depth of thick, high-velocity, potential reservoir formations in basins where the rock succession is inadequately known.

Seismic Reflection

The reflection method, which works on the echo sounding principle, is now an absolutely indispensable tool for oil and gas exploration, and gives more geological information than any other method. It is able to record reflected shock waves from a number of beds in a rock succession, and their angle of inclination, along the line of observation. The results obtained depend on the lithology, more reflections being obtained from thin-bedded strata than from massive strata. The records build up a vertical picture which gives a direct impression of the arrangement of the strata as in a geological section line. Reflection surveys down the dip of the strata or along the strike are easiest to interpret and give the maximum geological information. When dip and strike are not known they must be found by shooting reconnaissance lines.

A considerable expertise has developed in the methods for creating the shock waves, which can now be done by weight dropping and other vibration inducers in addition to explosives. The amount of geological information gained has also increased greatly in recent years, by many improvements in the processing techniques due to electronics. In marine areas, where special ships allow rapid surveying, and the presence of water as the medium for inducing the shock waves has advantages, remarkably good results are often obtained. The sparker and boomer methods of survey, which developed from the hydrographic echo sounding surveys when it was discovered that echoes could be obtained from the base of the superficial sediments, may in some areas be of great use in delineating geological structure in the first few thousand feet of strata below estuarine and marine areas. It is now possible to identify minor rock formations such as buried sand banks, minor structures of sedimentary origin (such as those caused by slumping before compaction), and also changes of lithology, in addition to the structural features on which boreholes are located.

The interpretation of seismic reflection survey records in terms of the known geological succession requires close co-ordination between geologists and geophysicists. Many assumptions have to be made when an area is first surveyed, in attributing reflections to particular formations. As geological and velocity data become available from boreholes all early interpretations have to be checked, and if necessary revised. How formidable this task may become is illustrated by the fact that some of the major companies working in the North Sea possessed in 1969 over 40 000 line-miles of observations in that area alone; this figure is now, of course, considerably greater.

Oblique Asdic Surveys and Submersibles

In the same way as oblique air photographs can be used to aid the study of the geology of land areas (Fig. 13) the oblique asdic apparatus now makes it possible to study the nature of the bottom in marine areas. This is a scanning echo sounder which gives a record along a wide strip of the bottom as the ship moves along. The nature of the various irregularities of the sea bottom affects the strength of the echoes. For instance, a scarp facing the echo sounder will give a strong echo, whereas the corresponding dip slope will give a weak echo. A bouldery bottom will give a different type of echo from a muddy or sandy bottom. The oblique asdic, or sonar as it is sometimes called, produces a record

Fig. 13. Oblique air photograph of geological structures. Two anticlines separated by a syncline can be seen in the centre and other anticlines in the distance. The hard, feature-forming formation is the Asmari Limestone. (Photo: Hunting Surveys Ltd.)

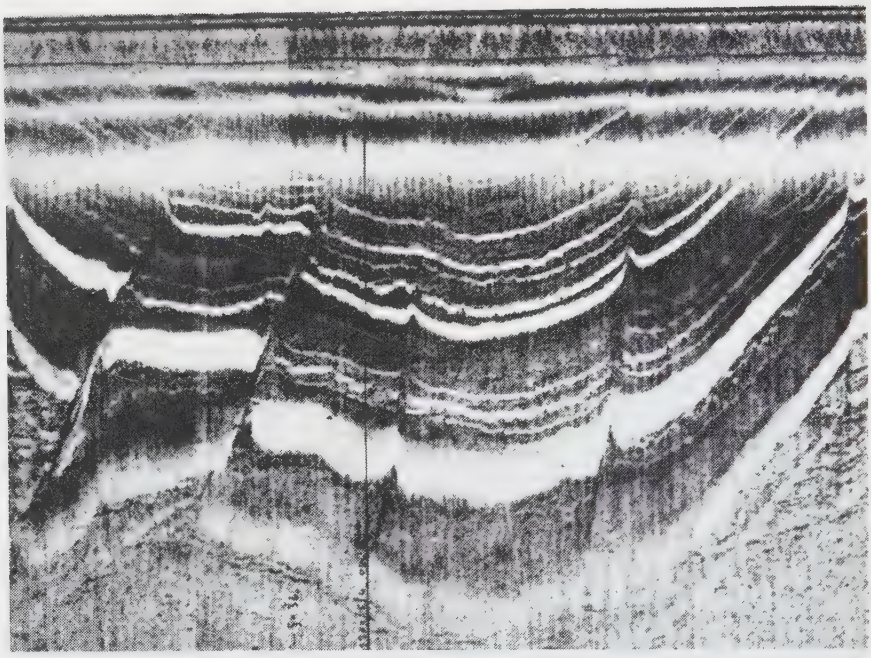


FIG. 14. Oblique asdic view of sea bed.

which can be of great value in sea-bed mapping or as a guide to subsequent sampling by diving or drop coring. Fig. 14 is a photograph of an asdic record of a patch of rocky sea floor about 800 yd wide mapped by a side-scan asdic from *Discovery II* on a 2-mile easterly traverse along the middle of the English Channel, south of the Isle of Wight. The pattern of Kimmeridge-type rocks can be seen because of differential erosion of the soft layers between stone bands. Outcrops are slightly curved, have a gentle northerly dip towards the ship's course and are broken by small faults. Bedding surfaces appear as darker tones than the shadows cast by scarp faces, which can be followed from plan view to section view beneath the ship.

Submersible vessels are now available which allow direct geological observations to be made on continental shelves and slopes as well as in shallow waters. These can be hired to obtain important data unobtainable by less costly means.

GEOLOGICAL SUCCESS AND ECONOMIC FAILURE—WHEN TO STOP?

Those concerned with the problem of estimating oil and gas reserves, and with evaluating published statements of oil and gas reserves, are very conscious of the difficulty of defining an exploration success. It is not uncommon for an oil or gas discovery to be a satisfying success to the exploration staff concerned but an economic failure to the organization which financed it. The gasfields discovered in the 1950s in Papua, not yet exploited, are an example of this. A kind of exploration success can be achieved by speculating in land values, by

selling interests, by obtaining royalties and by other devices which leave the real work to others, but real economic success is determined by the ability to find and produce oil and gas at a profit in all the circumstances existing in the area at the time. The economic problems which control this are of great interest to production departments, and no explorationist can afford to ignore them when making initial or final recommendations for action. There was, for example, an excellent case for searching for gas in the North Sea after the Groningen discovery but the case for deliberately searching for oil was unaffected. And the case for continued exploration is altered as economic factors are superimposed on the geological factors. George C. Hardin and Karl Mygdal have described the type of financial analysis which should accompany estimates of profitability in the production of oil and gas in an article entitled 'Geologic Success and Economic Failure' (see bibliography). An exploration organization has to look forward to a rate of return on its investment which is proportional to the calculated risks, or it will do better to invest in trustee securities. Hardin and Mygdal give an example of an economic failure in oil-rich offshore Louisiana where production is controlled by allowable production regulations. They made the following estimates for minimum economic success: Cook Inlet, Alaska, 5000 barrels per day production from one offshore drilling platform; Alaskan North Slope, 500 million barrels of recoverable oil; Canadian Arctic Islands, 2000 million barrels of recoverable oil.

As all geological appraisals are to some extent subjective it may prove more difficult to decide when to stop an exploration campaign than when to start it. If funds or enthusiasm run out the normal procedure before final withdrawal is to arrange a farm-out to some other exploration organization which has the funds, or is prepared to take greater risks. In this case an interest in any future discovery is often retained in return for surrender of the explorations assets, i.e. all the data so far obtained. Or a partner may be found to inject more funds into the venture in return for a share of future finds, or the assets may be exchanged for trading assets, or sold.

THE FUTURE

The future of oil exploration is obviously affected by the availability of undiscovered reserves, the cost of finding and developing these reserves, the future demand for oil, and the availability and price of alternative sources of energy and petrochemicals, etc. The history of the last few decades, the lack of any obvious breakthroughs in the development of new power resources, and substantial reductions in price of alternative energy, such as nuclear energy, and of alternative oils derived from coal, oil shale, etc. all lead to the conclusion that the demand for oil will go on increasing at rates similar to those of the past few decades. In view of the complicated relationship of economic factors that determine future production rates it is unrealistic to assume that a precise figure can be derived.

The historic rate of increase in demand of 7.5 per cent per annum, indicated in the early 1970s, might have appeared to be a realistic basis for future projections of oil requirements; events now show the risks involved in extrapolating curves. On that basis a quantity of oil equal to the indicated

reserves, calculated on the 1970 recovery factor, would have been consumed between 1970 and the mid 1980s. A comparable projection to the end of the century would have required something like four times as much as the reserves of the early 1970s to be found to accommodate the production up to the end of the century and to have sufficient in the ground to produce within reasonable economic limits at the high rates predicted then to obtain. Improvements in recovery factors would seem unlikely to change these estimates significantly. However, the spectacular rise in the price of oil triggered in 1974, coupled in recent years with the trade recession and other factors such as conversation, has led to the 1981 world consumption of oil being 2901.7 million tonnes, instead of some 4895 million tonnes which would have been predicted from the 1973 rate and a 7.5 per cent per annum increase. World consumption in 1981 showed a 3.3 per cent fall from the 1980 consumption (2901.7 million tonnes as compared with 3001.5 million tonnes) according to the estimates in the BP Statistical Review of World Energy.

If we examine the distribution of existing reserves and discoveries, and the oil prospects as they now appear, it would seem that there must be considerable doubt, on geological grounds, as to the availability of future reserves of the magnitude required if consumption is going to rise again at the rate achieved in the early 1970s (oil from shale and oil sands are not included in the estimates). Recent discoveries of gas in the Arctic, USSR and the Middle East have attracted attention, but it must be remembered that the oil equivalent of gas is low (28 300 cubic metres of gas are equivalent to 24.4 tonnes of heavy fuel oil). Geological data do not suggest that onshore or continental shelf reserves, proved, probable or possible, can maintain for long even present rates of consumption without the assistance of oil shale, oil sands and other syn-crudes. Optimistic estimates of the hydrocarbon prospects of unexplored deep-sea basins are geologically unjustifiable until bore holes have obtained essential data on their sedimentology. For example, the offshore basins around Antarctica which have attracted attention recently may be relatively poor prospects for sedimentological reasons.

As was pointed out frequently in articles published some ten years ago, a large proportion of the then known reserves were concentrated in relatively few fields and in few areas. About 78 per cent of existing proved reserves were concentrated in 161 oilfields, and some 60 per cent of those reserves were in a small area centred on the Persian/Arabian Gulf. Enough work had been done in most of the onshore sedimentary basins to suggest that prolific areas such as the Gulf were unlikely, and there was some evidence to suggest that we were entering the phase of oil exploration in which the average fields found would be progressively smaller. The two main implications of that trend were that considerably more effort would be required to locate the smaller and less obvious traps, and that because they would be found in increasingly more hostile environments, both onshore and offshore, the costs of exploration and production would rise.

Ten years of active world oil exploration have not necessitated any changes in that general assessment of the future oil situation. The BP Statistical Review of World Energy at the end of 1981 gives total world 'published' proven crude oil reserves as 92.1×10^9 tonnes. Of this 49.3×10 tonnes is in the Middle East, 74.5×10^9 tonnes is in the Eastern Hemisphere and 17.6×10^9 tonnes

is in the Western Hemisphere. The most significant increase in the Western Hemisphere has probably been in Mexico which now has proven reserves of about one seventh of the Middle Eastern total (Bull. A.A.P.G., October 1981). Of relatively explored areas China's southern offshore takes a prominent place, but a considerable number of North Sea or Alaskan sized areas would be required to maintain the economies of the oil-consuming industrial world, even at present growth rates. The consumer demands of a rapidly increasing world population for oil and gas is a long-term situation which will not go away. The economic slow-down at the present time has stimulated and is encouraging R & D for alternative, non-fossil, energy sources (earth and solar heat, wind, waves, biomass, etc.), and for more efficient energy use and conservation: short-term falls in oil prices must not be allowed to cause any relaxing of these efforts.

The general outlook for oil and gas exploration is therefore one of increasing activity, with increasing emphasis on detailed geophysics, and geochemistry, to locate smaller and more subtle traps. Another prospect that faces the industry is the tremendous capital requirement for finding and developing the oil needed for the future, particularly from offshore.

EPILOGUE

A fitting conclusion to this chapter is the following quotation from the end of the exploration chapter in the third edition of this book.

'The exploration and production of oil and gas involve great financial risks and require large financial reserves. Enormous amounts of money, as much as several hundreds of millions of pounds, may have to be spent before any return on capital investment can be expected. It may take years before the presence of commercial quantities of oil or gas in an exploration area can be proved or disproved. Consequently the exploration effort has to be planned long in advance of the time when production is actually required, which again depends on world supply and demand. Also, to reduce the overall financial (and political) risk, it is desirable to spread the effort over a large number and variety of prospects. This can only be realized by a large organization with a considerable backing of capital.

'The necessary funds to safeguard future exploration and consequently the future supply of crude oil and gas are such that they will be difficult to find, unless the oil companies put aside a great part of their earnings for this purpose. And even then it will not always be possible to explore all promising prospects and a selection will have to be made. As it is never known whether oil is present until it is found, this selection is always something of a gamble. It is the task of geologists, geophysicists, and other specialists to minimize this gambling risk.'

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I. P. Petroleum Statistics, with 1980 totals.

There is a vast, ever increasing oil geological literature. The monthly Bulletin of the American Association of Petroleum Geologists, for example, contains over 200 pages, approximately 2500 pages a year, and most papers published therein contain lists of references. The Association also publishes important special volumes on specific topics (e.g. Stratigraphic Traps; Habitat of Oil). The August volumes of the Bulletin contain an annual summary of exploration developments in countries outside the USA, from 1964 to 1970; corresponding material appears in the September issues in 1971 and 1972, and in the October issues from 1973 onwards.

The Proceedings of the ten World Petroleum Congresses already held are another mine of useful information.

3

Geophysical Methods Used in Prospecting for Oil

By J. MILSOM and G. B. MATTHEWS

INTRODUCTION

WHERE the deep geology of an area cannot be determined by conventional geological methods, either because the structures mapped at the surface are not related to those beneath unconformities at depth or because a cover of soil, sand, or water makes surface mapping impossible, other techniques must be used. Most of these can be described as geophysical, in that they make measurements of a physical quantity the basis for deductions about the buried geology. Some of the measurements are of natural phenomena, such as gravity and magnetic fields, and these provide useful but usually ambiguous information. Alternatively, the response of the earth to an artificial stimulus may be observed; the most important of these methods is seismic reflection, which makes use of sound or 'seismic' waves travelling in sedimentary rocks from an impact or explosion.

A medical analogy may be used. A good doctor can make a fair diagnosis on the basis of observation and the answers to questions about a patient's condition; this corresponds to the measurement of natural fields. Fairly soon, however, the limits of these techniques will have been reached and in medicine it becomes necessary to probe the body with X-rays or ultra sound, just as in geology the earth must be probed with seismic waves. Eventually it may be desirable to resort to the knife on the body or the drill on the earth. There is even a further possible stage, since the results of surgery may be ambiguous without still more instrumental tests; in the same way, to gain the maximum of information from a bore-hole, geophysical instruments may be lowered into it to make measurements from within the rock mass.

Seismic reflection work absorbs more than 95 per cent of all the money being spent on exploration prior to drilling. Because of its importance, this method is considered first and in the most detail. Magnetic and gravity surveys, which usually precede seismic work in an exploration programme, are considered in later sections, as is well logging, the final phase.

SEISMIC REFLECTION METHOD

All seismic methods are based on the ability of rocks to transmit elastic 'shock' waves, which are similar to sound waves in air and are commonly known as seismic or acoustic waves.

A sedimentary section consists of a number of layers of rocks with differing physical properties. The interface between two layers will reflect a portion of any acoustic wave incident upon it. By generating an acoustic wave at or near

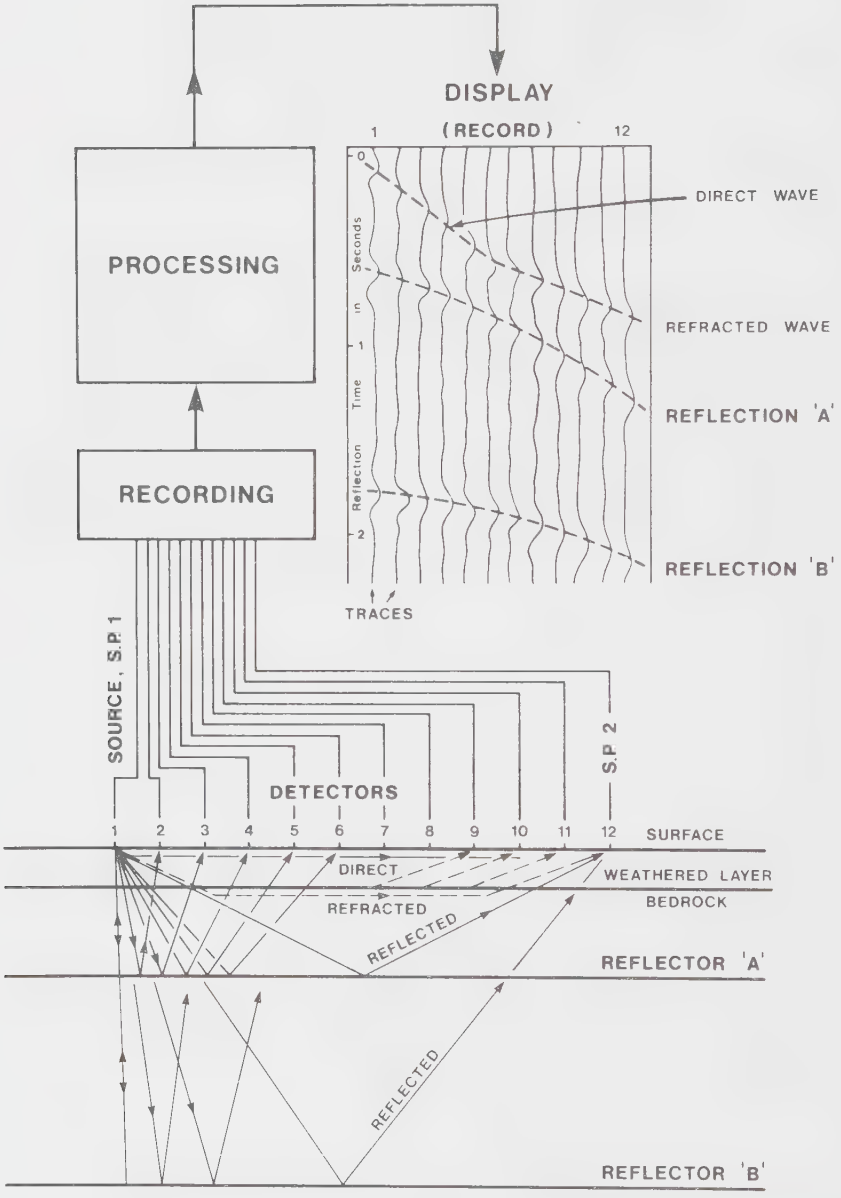


Fig. 1. Schematic diagram of the traditional seismic reflection survey.

the surface of the earth and measuring the vibrations over a few seconds it is possible to determine the time it takes for the wave to travel to an interface and back. If the velocity at which the wave travels is also known, the depth to the interface can be calculated. By repeating this process at a number of points on the surface, cross-sections or maps showing the structural attitude of the interface can be constructed.

The basic concept of reflection seismography is simpler than that of some other geophysical methods, but many serious problems must be overcome before useful information can be obtained. First, the reflections, or 'signals', are not in most cases the strongest events registered by the detectors, but are buried in a mass of irrelevant vibrations collectively known as seismic 'noise'. Some of the noise pulses are caused by waves which travel from source to detector by routes other than the simple reflection path and some are caused by such things as wind or traffic. Most of the technology involved in reflection seismography is aimed at the suppression of the unwanted noise, and the recognition and enhancement of the signal.

Another problem is that the seismic wave consists not of a single sharp event, but of a few cycles of compression and rarefaction covering a period of time which is often greater than the transit time between reflectors. This causes overlapping of the signals from closely spaced reflectors, making their recognition difficult.

Furthermore, the velocity at which the wave travels varies widely and may not be known. Nor can it be calculated from an experiment involving only a single shock and a single detector. Also, the reflection point in such an experiment would lie midway between source and detector only if the reflector were horizontal, and more complicated procedures are needed to allow for dipping beds. Clearly, much has to be done before useful information can be extracted from recordings of vibrations detected at the surface.

Historical Review

The first successful trials of the reflection seismograph were made in the early 1920s and it rapidly developed into a popular exploration tool. For about thirty years the improvements in the method were gradual, involving mainly the design of more sensitive detectors and recording equipment. From 1930 until about 1960, Fig. 1 would have served as a fairly complete picture of a reflection survey.

The source was explosive placed in a shallow bore-hole, the detectors a series of seismometers (geophones) laid out at regular intervals over a distance of perhaps a quarter of a mile. Recording was done by photographing deflections of a multi-channel oscillograph on a moving film. Timing lines controlled by a tuning fork were printed on the film every 0.010 second.

The record obtained by one shot into one spread of geophones was similar to that shown in Fig. 1. By shooting at shot-point 2 at the other end of the spread it was possible to read a reflection time at shot-point 1, follow it to shot-point 2 and read another reflection time. It was customary to use only the reflection times at the shot-points for mapping purposes, the other traces serving as a means of following the reflection from one shot-point to another.

The principles of wave propagation were well understood and the theoretical

bases of many of the procedures which are in use today were developed very early. The problems of noise and signal overlapping were recognized and many attempts were made to overcome them. Unfortunately the technology necessary for success was not available. The filtering of signal from noise by means of electrical circuits was not very satisfactory, and the photographic recording of the trace precluded further processing. In retrospect these methods seem cumbersome and inefficient.

In the late 1950s the recording of seismic traces on magnetic tape in analog form was introduced. It was a significant improvement over photographic recording in that it permitted subsequent processing. Magnetic-analog recording was common for a few years, but soon gave way to digital systems.

In a very short period of time, around 1960, there were two developments which together transformed the reflection seismograph from a useful but frequently unreliable exploration tool into a highly efficient means of gathering subsurface geological information. These were the Common Depth-Point (CDP) method of data gathering, and the application of digital techniques to seismic recording and data processing. The advantages which accrued can best be understood by considering the nature of seismic waves and the processing required to turn wave measurements into geologically useful sections.

Seismic Waves and Seismic Pulses

A discussion of the reflection seismograph requires some familiarity with wave theory and the terms used in the description of waves. A brief and much simplified review follows.

Waves are classified into two broad categories. Periodic waves, including such things as notes from a flute or the hum from a power line, repeat at precise intervals and can be recognized by the frequency with which they do so. Waves of the second type, such as booms and bangs, are of relatively short duration, have no recognizable frequency, and are not likely to repeat themselves within the time span under consideration. Their name of transient waves is also very descriptive.

An explosion or impact at or near the earth's surface generates two spherically expanding waves in rocks. The p- (primary, pressure, or 'push') wave is like a sound wave, with the particles moving parallel to the direction of propagation. In the s- (secondary, shear, or 'shake') wave the particle motion is at right-angles to the direction of propagation. It has no counterpart in fluids or gases.

The p-wave travels with the greater velocity, carries most of the energy and is the 'signal' in a normal reflection survey. The s-wave is important only as part of the seismic noise. Some research has been done into the possibility of using a comparison of p- and s-wave velocities as a means of determining porosity and fluid content in rocks, but, except possibly in the Soviet Union, such methods are not in routine use.

At interfaces between rocks of differing properties part of the energy is converted into complex elliptical waves known as Love waves. These are of negligible amplitude except at the interface between bedrock and unconsolidated soil, but associated effects can be important, since this interface lies only a few metres below the detectors. At the earth's surface another complex

wave, the Rayleigh wave, is also generated and in practice it is usually impossible to distinguish between Love and Rayleigh waves.

In discussing any waves it is necessary to distinguish between the particle velocity, which is the continually changing velocity with which a particle oscillates about its neutral position, and the transmission or propagation velocity which is the velocity with which the whole disturbance moves through the rock. Both velocities are important. The particle velocity activates the detector but the propagation velocity is the one used to relate reflection times to distances.

The speed at which a rock transmits the p-wave, known simply as the 'velocity' of the rock, is related to the density (ρ) and the effective elasticity (E) by the equation:

$$V = \sqrt{\frac{E}{\rho}}.$$

An important property of the rock is the acoustic impedance (I) which may be thought of as the resistance which the rock offers to the compression of the particles. It is calculated by multiplying the density by the velocity, so that the velocity varies directly with the impedance. The apparent contradiction is explained by the fact that it is the displacement of the particles which is impeded, not the transmission of the wave.

The relationships given above are for a 'perfect' solid and are approximately true for non-porous rocks composed of one mineral. Such rocks are rare. Sedimentary rocks are usually composed of a mixture of minerals and are porous to some extent. In practice, velocity and density can be measured, and acoustic impedance and elasticity are then calculated on the assumption that the relationships are workable approximations.

The variation in velocity for any one rock type is due almost entirely to variation in porosity. Depth of burial has little effect on velocity, and age none at all, except that it tends to reduce porosity.

There is no single velocity associated with any sedimentary rock type (except evaporites). Velocities form an overlapping spectrum with poorly consolidated shales and sandstones at one end, with velocities in the region of 1500–1800 m/sec, and dense carbonates at the other, with velocities in excess of 3500 m/sec.

Periodic waves

The movements of individual particles in a periodic wave are governed by the laws of simple harmonic motion, and the progress of the wave can be described by a sine or cosine formula. The vibration of a particle involved in a cosine wave can be related to a rotating vector as shown in Fig. 2. The vector rotates through 360° for each cycle of the wave and the number of rotations it makes in one second is the frequency of the wave, expressed as cycles per second or hertz. The angle between the vector and the starting position is called the phase angle (ϕ). The length of the vector (A) is proportional to the maximum particle displacement and the displacement at any instant is given by $A\cos\phi$. Two or more coexisting waves of different frequencies are said to be in phase when their

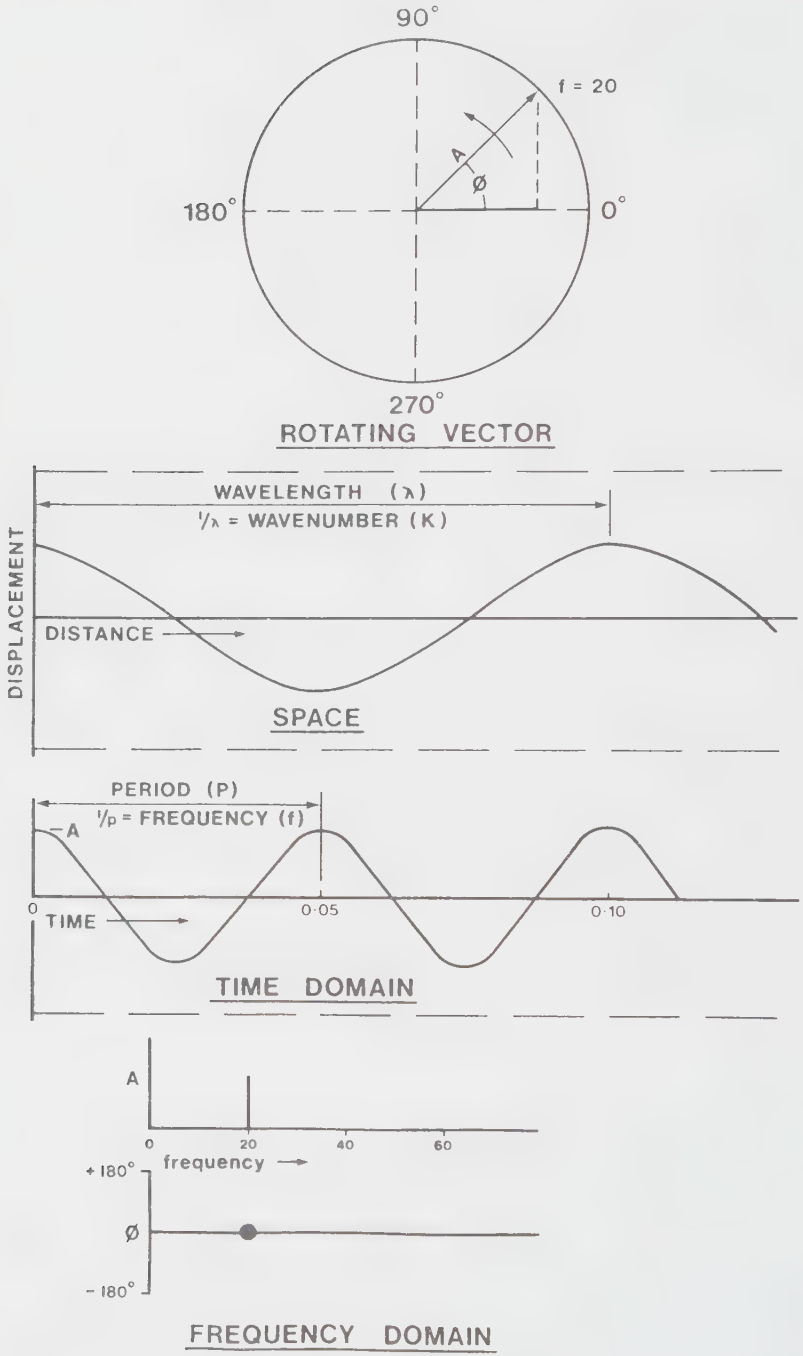


FIG. 2. Rotating vector and graphical representations of a periodic wave.

phase angles are equal; at other times they are out of phase by the angle between their vectors.

Waves can be described in terms of space, time, or frequency. At one stage or another it is necessary for the seismologist to consider them from each of these points of view.

If the wave is considered in space, it is necessary to specify the amplitude (A), the wavelength (λ), or its inverse, the wave number (K), the velocity (V), and the phase at some particular point. This view is equivalent to stopping time and observing the position of various particles over some distance.

If the wave is considered in time it is necessary to specify the amplitude (A), the frequency (f) (or its inverse the period, P), and the phase at some reference point in time. This is equivalent to observing the movement of one particle over a length of time.

A third way of describing a periodic wave is to plot its amplitude on a scale of frequencies and its phase at a reference time on the pair of diagrams known as the amplitude spectrum and the phase spectrum which describe the wave in the frequency domain. Obviously a great number of coexisting periodic waves can be plotted on one pair of diagrams.

It may be worth emphasizing that none of the illustrations in Fig. 2 is a 'picture' of the wave. All are descriptions of it in different frames of reference.

The seismic pulse

The seismic pulse is a transient wave consisting of a few alternating compressions and rarefactions, and so the relevance of periodic waves is not immediately obvious. The reason they enter the discussion is that in the analysis and manipulation of transient waves it is convenient to suppose that these are the result of the combination of a great number of coexisting periodic waves. Unlikely as it seems, theory predicts and experience confirms that any transient wave can be approximated to any degree of precision required, by summing the effects of periodic waves, provided that there are no restrictions on their number, amplitude, frequency, or phase relationship. However, the number of periodic waves needed for a seismic pulse is so great, and their frequencies are so closely spaced, that in effect they form a continuous spectrum.

Given a transient waveform such as a seismic trace it is fairly easy to break it down into its constituent periodic waves and represent it as a continuous spectrum in the frequency domain. In this form the transient wave is specified as a series of numbers corresponding to frequency, amplitude, and phase which lend themselves to mathematical treatment more readily than does the time domain description.

The procedure by which the description of the wave can be changed from the time domain to the frequency domain and vice versa is known as the Fourier transform. The time frequency transforms for a few simple waves are shown in Fig. 3.

The useful information on a seismic trace tends to be concentrated in a certain range of frequencies, usually between 10 and 80 Hz. Frequencies outside this range are likely to contain a high proportion of noise. The amplitude spectrum illustrates the frequency content of the trace and is useful

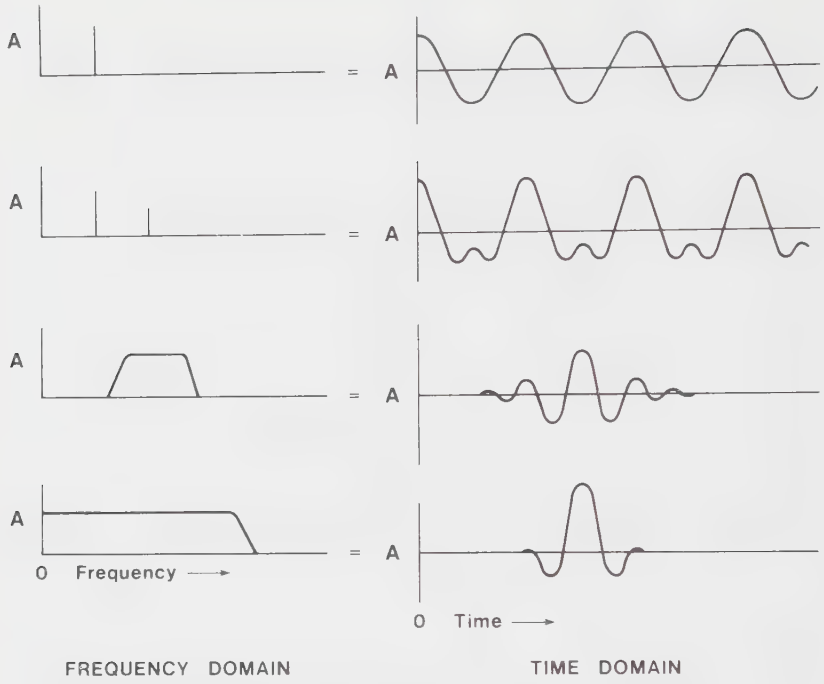


FIG. 3. Frequency domain and time domain representations of some simple waves.

in the design of filters which will pass only the desired band. At its inception the seismic pulse is thought of as consisting of the sum of all the frequencies within the range of the recording equipment, in phase at the shot instant. In fact the impact or explosion permanently disturbs the nearby rocks so that initially the pulse does not obey the elasticity laws which govern its behaviour later. However, it can be shown that after a short time it can be considered as the sum of a broad band of frequencies.

Attentuation and pulse lengthening

The wavefront expands spherically, and if transmission were perfect the energy per unit area would decrease with the square of the radius and the amplitude would vary inversely with the radius. However, a certain portion of the energy is dissipated as heat. This is known as absorption or attenuation. Energy is absorbed roughly as a fixed percentage per wavelength and consequently high frequencies are absorbed more than low ones over a given distance. The 'effective frequency' of the pulse is thus reduced and cycles are added to it. The new pulse, consisting of more cycles of longer wavelength, is less efficient in delineating small structures or resolving closely spaced beds.

If reflections follow one another at intervals of less than one eighth of the effective pulse wavelength, it is usually not possible to resolve them. The wavelength is of the order of 50 m during the first half second; after several

seconds it would be several hundred metres, so the decrease in resolving power is quite rapid.

As well as losses due to absorption, considerable amounts of energy are lost by reflection. The net combined effect of reflection, absorption, and spherical spreading is a very rapid decrease in intensity of the seismic signal with time.

The Composition of Reflections

When a seismic pulse encounters a boundary between rocks of differing physical properties, part of the energy is transmitted and part reflected, the proportions depending on the relative acoustic impedances of the rocks. The fraction reflected is expressed as the reflection coefficient (r), which for right-angle incidence can be calculated by the formula:

$$r = (I_2 - I_1)/(I_2 + I_1).$$

It will be recalled that the acoustic impedance (I) is equal to the product of density and velocity. In many cases the density of the rocks in the subsurface is not known, but the velocities can be derived from seismic data. It is then necessary to reduce the above formula to the approximation:

$$r = (V_2 - V_1)/(V_2 + V_1).$$

Since the densities of rocks vary within much narrower limits than do the velocities, the approximation is usually close.

What the seismograph 'sees' in the subsurface is a series of reflection coefficients, which may be positive or negative, spaced at irregular intervals of time. This is known as the reflectivity series.

At each interface a portion of the down-going pulse is 'folded back' to form part of the up-going train of reflections. In the case of a positive reflection coefficient the phase of the pulse is unchanged, but where the coefficient is negative the phase is reversed. Where reflector spacing is less than the length of the pulse the several up-going waves are superposed to form one complex composite wave as illustrated in Fig. 4. The seismic trace recorded at the surface consists of:

$$(\text{pulse}) * (\text{reflectivity series}) + \text{noise}$$

where the $*$ indicates the mathematical combination process known as 'convolution'.

Seismic Noise

Seismic noise falls into two broad categories. Coherent noise consists of waves which are generated at the shot point but which travel to the detector by routes other than the shortest one to the reflector and back. The direct waves, including the Love and Rayleigh waves which travel along the surface of the earth, are usually known as the 'ground roll', and are important sources of coherent noise. Other horizontally travelling waves may be reflected back from such topographic features as canals, river banks, or cliffs. Multiple reflections which interfere with primary reflections arriving at the same time are also important. They occur because the earth's surface, the base of the weathered

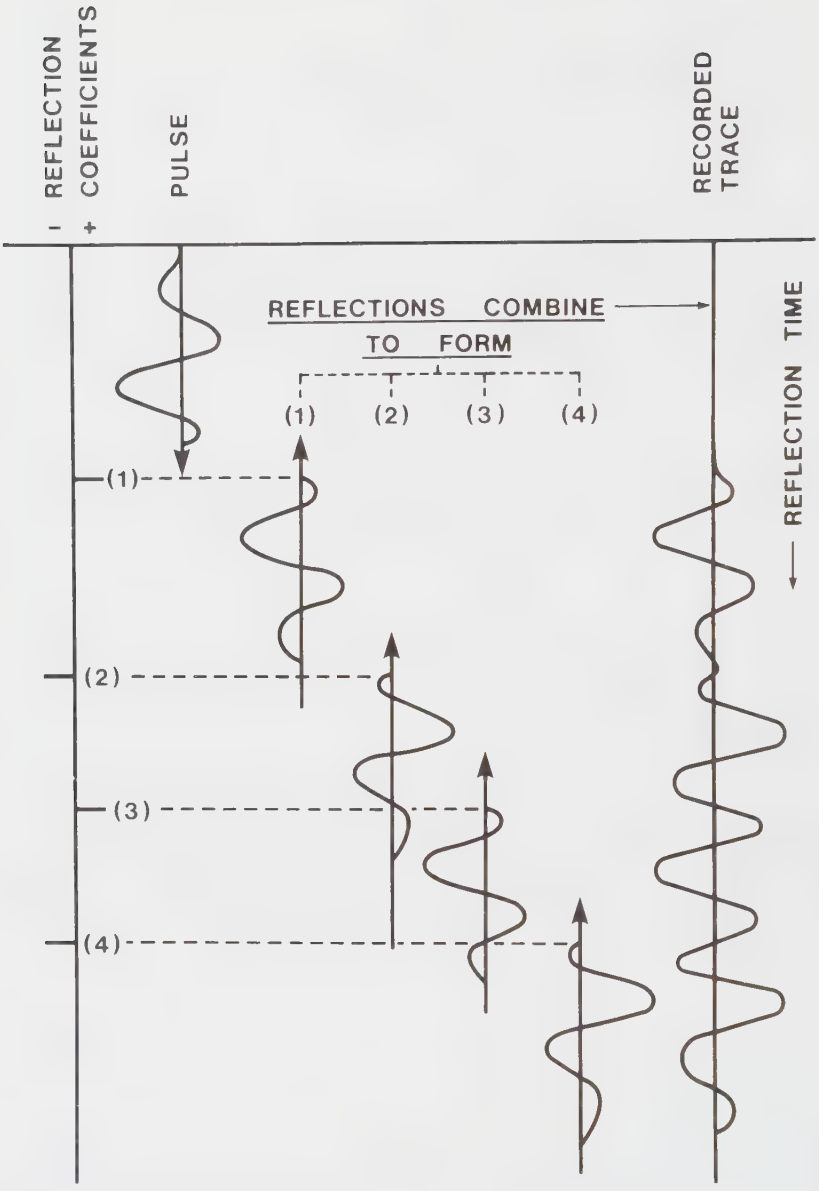


FIG. 4. The combination of reflections to form a seismic trace.

layer and, at sea, the air/water interface are all excellent reflectors, so that upcoming waves are turned around to make another trip. If the source is located beneath the surface, the upward travelling portion of the wave is reflected downwards from the surface and also sometimes from the base of the weathered layer, to follow the initial pulse as a 'tail' or 'ghost' a few milliseconds later. Other waves travel by complex routes involving both reflection and refraction.

Discontinuities in reflectors or sharp folds act as 'point reflectors' giving rise to 'diffraction' hyperbolae which obscure the details of highly folded or faulted structures. Fortunately, most coherent noise has characteristics which distinguish it from primary reflections and can be greatly reduced by proper field and processing techniques.

The second category, random noise, is a catch-all term for noise which cannot be correlated between traces, for which no pattern can be recognized and which is not related to the seismic impulse. Natural ground vibrations, wind and movements of people, animals, or machinery in the vicinity of the survey are some of the main constituents. Much random noise falls in a higher frequency range than the primary reflections and its effects can be reduced by frequency filtering. However, since it is not related to the source, its amplitude remains constant while the pulse decays, and it always prevails in the end.

Data Acquisition

Sources

The traditional source of a seismic pulse is a charge of explosive in a shallow bore-hole. It is the most efficient method of getting seismic energy into the ground and is still widely used. However, its use presents safety/security and environmental problems, and there have been many attempts to find alternatives. None have been successful in generating comparably powerful pulses, but the advent of magnetic recording has made it possible to sum several small pulses to achieve the effect of one large one. With this flexibility a number of sources have been developed which match the efficiency of explosives while avoiding most of the undesirable side-effects.

The simplest of these is the 'thumper' or weight-dropping method. A weight of two or three tons is lifted to a height of about three metres and dropped, generating a small seismic pulse. The record is stored on magnetic tape and added to the result of previous 'thumps'. The procedure is repeated until the required level of energy in the signal is achieved. Analogous methods, with small explosions contained in cylinders in place of the weight drop, are also in use.

Another and increasingly popular seismic source is the Vibroseis (TM) (Fig. 5). In this method a plate in contact with the ground is made to vibrate through a range of frequencies in a continuous sweep lasting several seconds. In processing, the recorded trace is cross-correlated with the input signal, producing a correlogram which is similar to the trace which would have been obtained with a 'spike' type source. Several 'sweeps' are necessary to build up a signal of sufficient strength. Among the advantages of the method are the control available over the frequency content of the signal, the relative insensitivity to ambient noise, and safety in use in built-up areas.

Dynamite was also the first source used in marine work but the oscillation of the bubble results in a long and complex pulse which is unsatisfactory. Explosions are also very damaging to marine life. For these reasons alternative methods were soon developed.

The airgun, which releases a charge of compressed air into the water is the most popular marine source at present. It has the advantages of being efficient

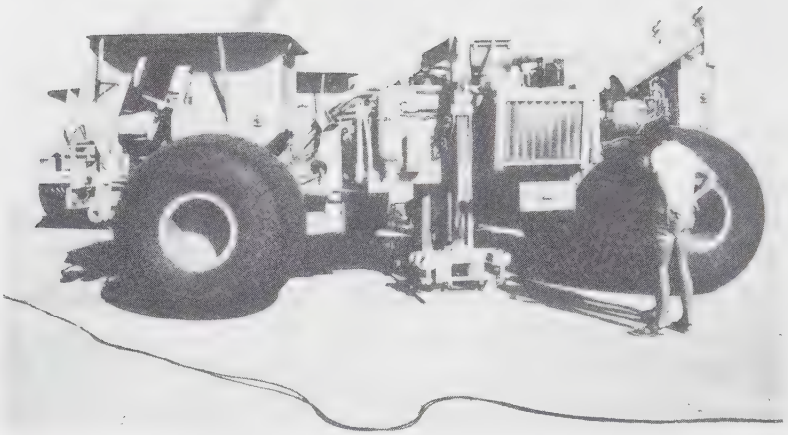


FIG. 5. Vibroseis (TM) Birdwagen seismic vibrator in Libya for Seismograph Service Ltd. (Photograph by courtesy of A. K. MacKenzie.)

and not requiring the transport and storage of explosive materials. Waterguns rely on implosion, i.e. the rapid collapse of an underwater cavity, and are claimed to produce a very short 'spike' pulse.

Several methods involving contained or damped small explosions are also in common use. These include the sleeve exploder, in which the explosion is contained within a flexible sleeve, and the Flexotir (TM) in which the explosion takes place within a perforated metal sphere. The Vaporchoc (TM) utilizes the implosion of a bubble of superheated steam to generate a pulse.

In surveys requiring only shallow penetration, such as oceanographic research projects and site investigations for drilling platforms, sparker systems are a popular source. This method generates a small high-frequency pulse by a high-voltage electrical discharge through the sea water. Magnetostrictive devices known as 'boomers' have similar characteristics.

Whatever the source, on land or at sea, it is customary to use a source 'array' rather than a single source point. The reason is that by judicious choice of the array spacing it is possible to direct most of the energy downward, where it is needed, as well as to achieve a certain amount of cancellation of the horizontally travelling waves which are an important element in seismic noise.

Detectors

The detectors used in land surveys, known as geophones, consist of a permanent magnet and a conductive coil, one of which is fastened to the frame from which the other is supported by a soft spring. When the geophone is moved the difference in velocity between the magnet and the coil generates a small voltage in the coil. The voltage is closely related to the particle velocity of the arriving seismic waves and its representation in the form of a wiggly line is what is referred to as the seismic trace.

In marine work the detectors are known as hydrophones and consist of piezoelectric transducers which generate voltages in response to pressure changes. They are contained in a neutrally buoyant 'streamer' which is towed behind the recording ship, kept at a fixed depth by pressure-sensitive devices known as 'birds'. It will be noted that hydrophones are sensitive to pressure, whereas geophones are sensitive to movement. Consequently land and marine seismic traces do not represent exactly the same thing. In practice, the difference does not pose a serious problem.

As with sources, detectors are not usually used singly, but in groups or 'patterns'. Detector patterns also have a selectivity with regard to the direction, velocity, and frequency of arriving waves and can be designed to discriminate between signal and noise.

Recording

Recording systems ordinarily receive signals from 48- or 96-detector groups simultaneously. The amplitude of the signal from each terminal is converted into binary code and printed separately on tape, each sample occupying one line. Thus in a 48-channel system the samples from channel 1 would occupy lines 1, 49, 97, etc.

In order to compensate for the decay of the seismic pulse it is necessary to amplify the signal by a factor which increases with time. The degree of amplification can be controlled by a preset program or by a system which samples the signal over a short period and applies the required amplification. In either case the amplification factor is recorded along with the signal sample so that the true amplitude of the arriving reflection is known. It is then possible to present the seismic trace in such a manner that the amplitudes of successive reflections are proportional to the corresponding reflection coefficients. This step is essential to the analytical interpretation of seismic traces.

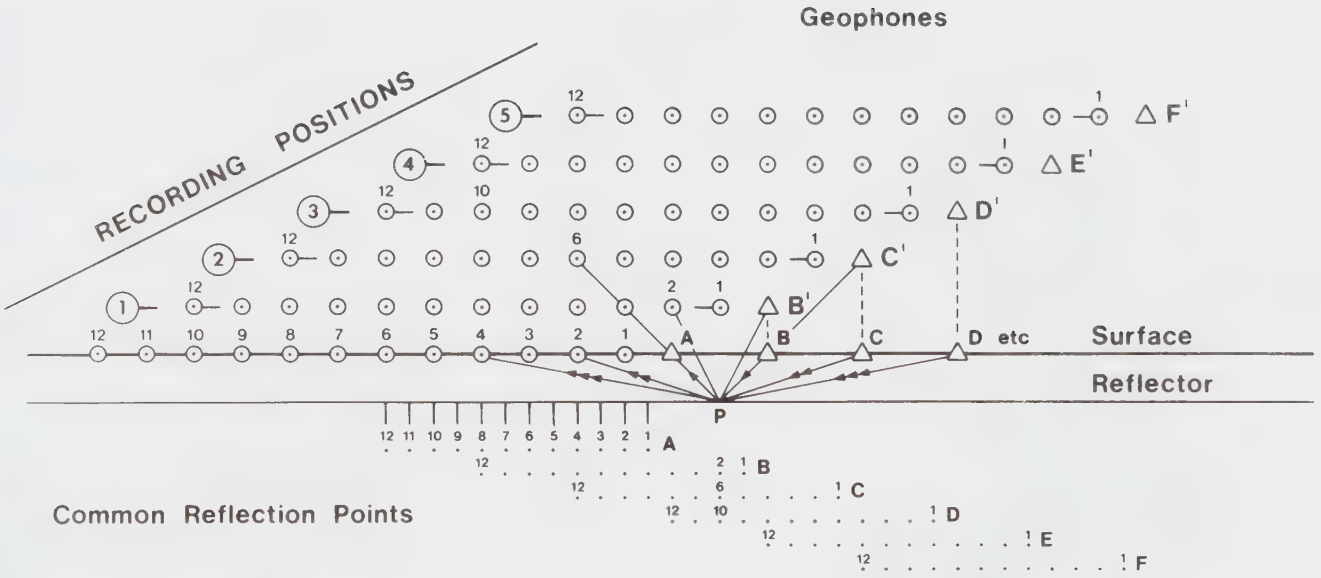
Sampling

The frequency with which the signal is sampled is critical because it determines the range of frequencies which can be recovered from the digital information. Signal frequencies of less than half the sampling frequency can be recovered, but higher frequencies will be passed as an aliasing wave of lower apparent frequency. This is an undesirable effect, and to avoid it an anti-aliasing filter which rejects the higher frequencies is applied in the field before sampling.

A sample period of 0.004 s ($f = 250$) will pass all frequencies up to 125 Hz without aliasing and this is usually sufficient. In special cases a period of 0.002 s may be used, but this doubles the amount of data to be handled and the increased cost is not always justified by the marginal improvement in data quality.

Land field procedures

Data acquisition on land is preceded by the geodetic surveying of lines to be shot and the flagging of reference points, or stations. Sections of multiconductor cable are laid along the lines with electrical take-outs at the stations where



3 - Fold C.D.P. Coverage

FIG. 6. Principles of common depth point coverage.

geophone groups are connected to the cable. The recording unit is connected to the cable through a junction plug with one conductor corresponding to each station.

Land operations permit flexibility with regard to source and geophone arrays, so the first step in a new area is usually a noise analysis to determine the characteristics of the seismic noise. A cable is laid out with relatively short station spacing and the geophones are bunched at each station. A shot is fired at one end of the spread and if necessary at several points displaced from the end of the spread. A display of the resulting traces makes it possible to determine the frequency, wavelength, and velocity of all waves which are recorded, and to identify which are primary reflections and which are noise. Source and geophone arrays can then be designed to discriminate against the noise.

In routine operations several sections of cable are laid out with station spacings of the order of 50 m and with the appropriate geophone arrays at each station. The number of stations is considerably greater than the recording unit can handle at one time, but a switching device ('roll-along switch') allows selected traces to be recorded. Recently methods have been developed whereby the signal is digitized at the geophone group and is then transmitted to the recorder either by radio or along a pair of conducting wires.

The source moves along the line 'shooting' the required pattern at stations which have been chosen according to the density and 'fold' of coverage desired. Figure 6 illustrates the steps necessary to obtain what would be termed threefold coverage. Suppose that twelve channels of the recording system correspond to cable take-out positions 1 to 12. In recording position 1, a shot at station B will result in a reflection from point P being recorded on channel 2. In recording position 2, a shot at station C will result in a reflection from the same point P being recorded on channel 6; similarly with station D and channel 10. The three traces thus obtained comprise a threefold CDP gather. Corrected for the path length differences and added together they form a single threefold CDP trace for station A. By repeating the procedure for each station on the line, a threefold CDP seismic section is obtained. Increasing the 'fold' of the coverage increases the cost of the survey, which must be weighed against the expected improvement in data quality. Twelve- and 24-fold are in common use in land surveys, the maximum fold attainable being equal to half the number of channels employed and being attained when the interval between shot points is the same as between geophone groups.

Marine field procedures

Positioning poses a special problem in marine surveys. Radio-positioning systems are used where possible but they are not effective at distances greater than about 500 km from shore. Beyond that a combination of satellite navigation and Doppler-sonar systems provides positional control. The precision of these systems is not as high as that of land-based geodetic surveys, but errors usually do not exceed 100 m and this normally suffices.

A marine crew would have available only a fixed source-array and possibly a choice of two or three streamers with different station spacings and detector patterns, and so lacks the flexibility of a land crew. On the other hand, the ocean is free from the near-surface variations which plague land operations,

and water does not transmit the shear wave, so the noise problem is not so severe. Consequently, marine seismic data are usually of much better quality than land data for areas of equivalent sub-surface geology.

Except for the shore-based beacons of the radio-navigation system, a marine crew is a self-contained unit. The navigational and recording equipment as well as the digital computer which serves them are all built into the ship. A frame on which the source elements are mounted is attached to the ship, and the streamer containing the detectors is towed behind. Forty-eight or 96 channels are customary, with detector groups spaced at something of the order of 50 m.

The ship cruises at a steady speed of a few knots and the source is activated at intervals which are determined by the 'fold' of the coverage desired, usually 24 or 48.

In areas where ocean currents are strong the streamer may not track the ship but may 'feather' out behind it at some angle. This angle can be measured by means of marker buoys on the streamer and can be recorded with the rest of the navigational data. Adjustments can then be made to the data base map so that the reference points correspond to the actual detector locations at the time of the shot.

Data Processing

The high-capacity digital computers needed to process seismic data are, together with the necessary disc and tape drives, too large to be portable. Consequently, processing is done in permanent centres which are often far removed from the survey areas. The various processing operations are discussed below in roughly the order of execution, although it has to be remembered that some, such as frequency filtering, are repeated in slightly different forms at more than one stage in the sequence.

De-multiplexing

Seismic data are normally written on field tapes in multiplexed form, that is the signal strength sample values are recorded for all channels at a given sampling instant before any values are recorded for the next instant. Before any analysis can be done, these values must be sorted (de-multiplexed) on to an edit tape as continuous traces for the individual geophone groups.

Filtering

The level of random noise on a seismic trace is normally fairly constant, whereas the signal and the coherent (source-generated) noise decay rapidly. Consequently the signal will always eventually disappear below the noise. If this occurs before the base of the sedimentary section has been reached, means must be found to increase penetration. One way of doing this is to reduce the noise level by filtering, which can be effective since the random noise tends to be composed of frequencies higher than those associated with the signal. This is especially true of the later stages of a record, since the high-frequency content of the signal is rapidly attenuated, and time-variant filtering (TVF) is often employed.

Static corrections

Land surveys are made on a surface of varying elevation which overlies the weathered zone, an irregular layer of generally low velocity. Corrections must be made both for the low-velocity layer (LVL) and for the elevation variations, since each imposes a variable delay on times of arrival at the geophones. The sum of the two corrections involves a time shift of the whole seismic trace known as a 'static' correction, to distinguish it from the time-dependent 'dynamic' correction.

A one-way correction must be calculated for each detector station and shot-point, due allowance being made for shot-hole depth where explosives are used. The depth and velocity of the LVL are usually calculated from the arrival times of the direct and refracted waves from bedrock (together known as 'first kicks'), but where this method is not applicable specially designed shallow refraction surveys are carried out, as described later in this chapter. The elevation correction compensates for the difference in elevation between stations, and involves the use of a datum or 'replacement' velocity which may be determined from the velocity of the refracted wave from the bedrock, or from bore-hole information where this is available.

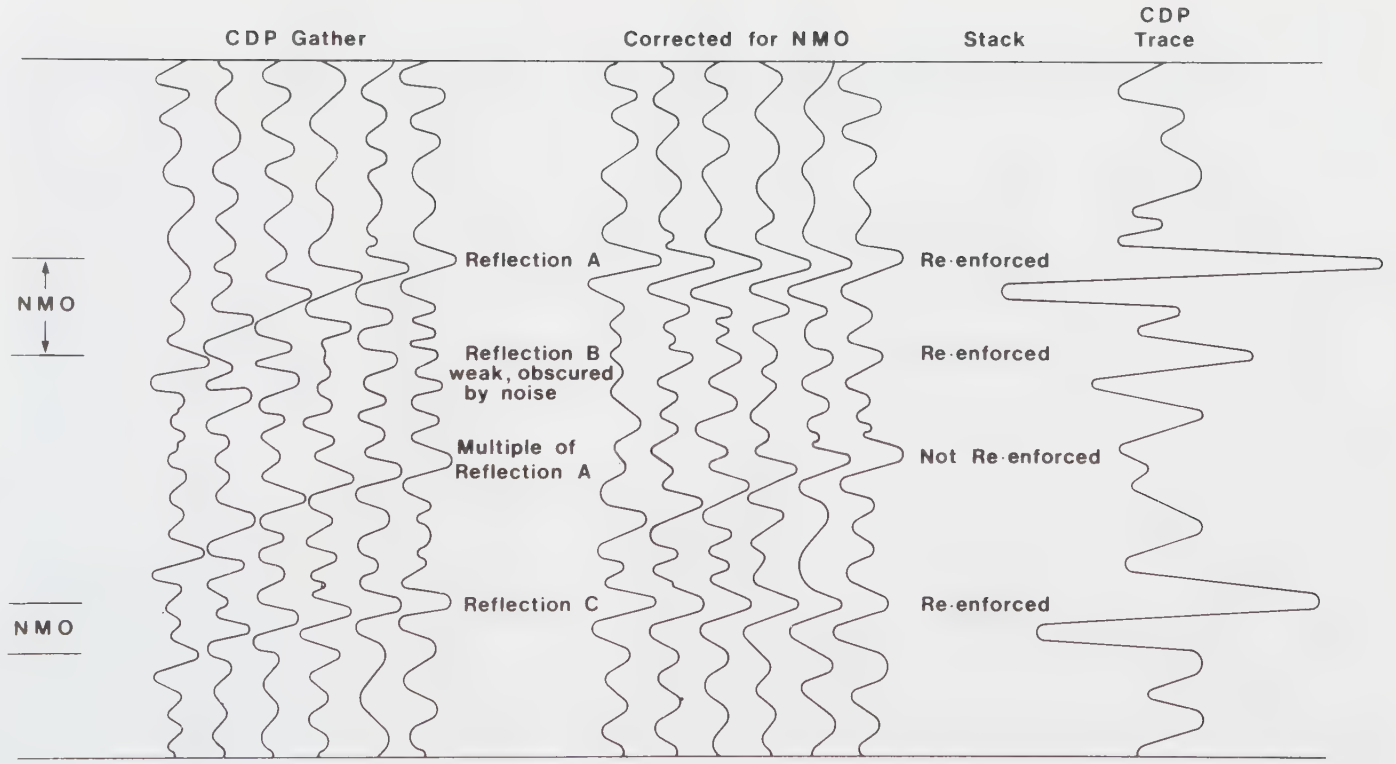
The 'field statics' determined by these methods are subject to error and in the data processing centre they are followed by residual or automatic statics in which adjacent traces are cross-correlated and time shifts for maximum correlation are applied. In marine work, or in land surveys where statics are assumed to be dependent on elevation only, field statics may be dispensed with. Because static corrections are likely to be different for each trace they must be applied before any of the steps in CDP stacking.

Dynamic corrections

The object of the dynamic correction is to compensate for the differences in ray path lengths caused by differences in offset distances (normal move-out or NMO) so that the traces of the CDP gather can be added together, or 'stacked'.

As can be seen on Fig. 7, reflections from a horizontal interface will form a curve (actually a hyperbola) on an uncorrected gather. In practice, besides the strong reflections which can be readily seen on the gathers, there are many other reflections hidden in the noise and the object of stacking is to reinforce these so that they emerge above it. This requires a dynamic correction for all times for each trace of the gather. Such corrections can be computed, provided that the way in which the average velocity changes with reflection time (or depth) is known.

Figure 7 represents a sixfold gather containing reflections, multiples, and random noise. The appropriate dynamic corrections will adjust the traces so that the arrival times for all the reflections are equal, and on stacking they will be reinforced by a factor of six. Multiples, having travelled a different route from the primary reflections, will have different velocities and different NMOs, and will tend not to 'stack'. The amplitude of the random noise will be increased by a factor of $\sqrt{6}$, with the result that the signal/noise ratio is improved by a factor of $\sqrt{6}$.



EFFECT OF STACKING

FIG. 7. Improvement in signal/noise ratio brought about by stacking.

Velocities

There are a number of methods for deriving velocity functions from CDP gathers. One of the simplest is the constant velocity scan. The NMO corrections for a constant average velocity of 5000 ft/sec are calculated and applied to the gather, the procedure is repeated for velocities of 6000, 7000, etc. up to perhaps 15 000 ft/sec. The displays are then examined for reflections which have been flattened by the corrections; if this occurs the velocity is appropriate for the reflection time. The time–velocity pairs so obtained are the control points for the velocity function. The method can be automated by computer programs which sum the amplitude of the reflections for each velocity, or which cross-correlate the traces for each velocity. The results are presented in several ways, one of the most popular being the contoured correlation display of Fig. 8. Another popular method is to stack a short portion of the seismic section with a spectrum of constant velocities; where reflections 'stack' the velocity is appropriate and the function can be built up as with the constant velocity scan.

Many seismic surveys are carried out before drilling, so the velocities necessary for stacking and interpretation must be derived from the normal move-out of reflections. Where a bore-hole is available, more precise velocities can be obtained from direct measurements. In a well velocity survey, or 'well shoot', a geophone is lowered into the hole and seismic shocks are generated at the surface with the geophone at a succession of depths. The travel time from surface to geophone is measured and the velocities can be calculated.

The sonic logging tool, also known as the continuous velocity logger or CVL, is used to provide a continuous record of the variation of velocity with depth in the bore-hole. It consists of a 'sonde' a few metres long, at the lower end of which is a transducer which produces a high-frequency signal. At least two receivers are mounted at different distances along the sonde to record the arrival times of the signal from the transducer. The first arrivals will be the waves that have passed along the sides of the hole, in the wall rock, rather than those which have passed through the lower velocity drilling mud, and two receivers are needed to eliminate the delay time introduced by the travel of the wave to and from the wall rock, through the mud. Logs are displayed in units of microseconds per foot or per metre, or as velocities, or both.

Although a high degree of accuracy is attained by the sonic log in the measurement of individual velocities, small systematic errors tend to accumulate if the results are used to calculate average velocities over large intervals, and the log should ideally be calibrated against a 'well shoot' survey. A difference also exists between the sonic log velocities and those with which useful seismic waves travel, because of the frequency difference; waves of different frequencies travel through rocks with slightly different velocities.

Deconvolution

An ideal seismic trace would consist of a series of 'spikes' corresponding to the reflection coefficients in the sedimentary section, but the seismic pulse consists of several cycles and often carries with it a tail of ghost events. This results in the overlapping of the responses from reflectors and it is often difficult to identify them even on filtered and stacked traces. The process of shortening the signal so that it comes closer to the ideal of a spike is known as deconvolution.

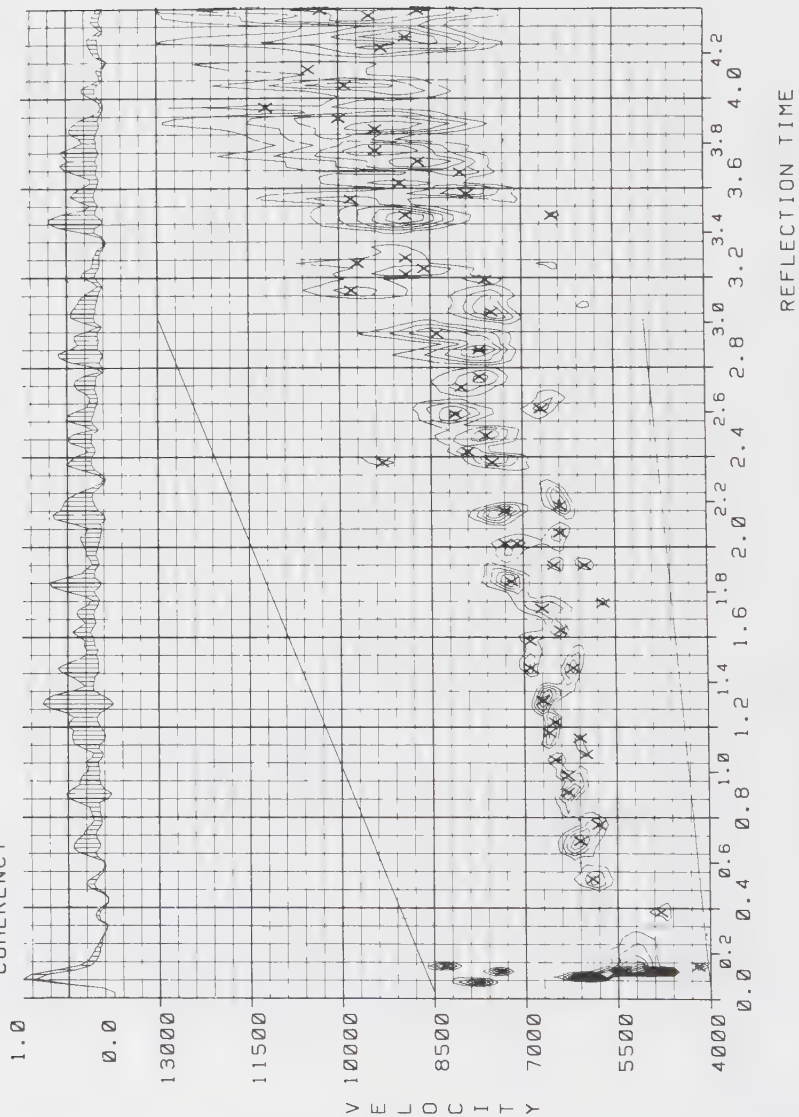


FIG. 8. Velocity analysis display of the 'knot-hole diagram' form.

The principle is best illustrated by the treatment of an intentionally long pulse, that from a Vibroseis. In Fig. 9 the frequency sweep of the Vibroseis is represented as a horizontal line (the down-going pulse). The reflectors 'fold back' the sweep as shown, that is to say, the pulse is convolved with the reflection series. The overlapping of the up-going reflected pulses results in a complicated trace which has no obvious relationship to the reflectors. However, if the pattern of the sweep is known and is cross-correlated with the recorded trace, the resulting correlogram will have peaks which correspond to the positions of the reflectors.

Deconvolution is performed in many different ways but is always aimed at relating a complex signal to a unique reflector. The presence of noise on the trace prevents perfect deconvolution and, except in the case of the Vibroseis, the exact shape of the pulse is not known. Nevertheless, deconvolution programs do shorten the signal and decrease overlapping. Traces can be deconvolved before stacking, after stacking, or both.

A mathematically similar technique, known as predictive deconvolution, is used to reduce the effect of multiple reflections. The locations and magnitudes of multiples associated with strong primary reflections can be computed. These computed signals can then be subtracted from the trace.

Migration

Unless the interfaces between different rock units are horizontal, reflection points will not be directly below surface point midway between the source and the detector group, and the reflector will therefore be wrongly located on the seismic section. Anticlines are made to appear broader and synclines narrower than is really the case. Very narrow synclines actually produce intersecting reflections from the two limbs, and there may be an apparent but completely artificial anticline beneath the deepest part of the fold.

Sharp discontinuities produced by faulting may also give rise to strong oblique events which appear on the seismic sections as hyperbolae with their apexes at the discontinuity. The hyperbolae are known as diffraction patterns, and may seriously affect interpretation in heavily faulted areas. Mathematical techniques exist by which oblique reflections may be 'migrated' to their correct places on the seismic section. Because information is usually available only from along the source-detector line, while many of the patterns seen are produced by 'cross-dip' from structures to the side of the line, migration can normally be done only imperfectly. Dipping reflectors will be migrated by different amounts on different seismic sections at intersection points, and so loops cannot be tied after migration. Migrated sections are usually not required in areas of gentle dip, although they may be justified on the grounds that they permit better definition of faults and unconformities.

Bent lines

When exploration is being carried out in topographically rugged areas, or in populated areas with an existing network of roads and field boundaries, seismic crews often find themselves forced to follow lines which are not even approximately straight, and processing centres have to be able to cope with this

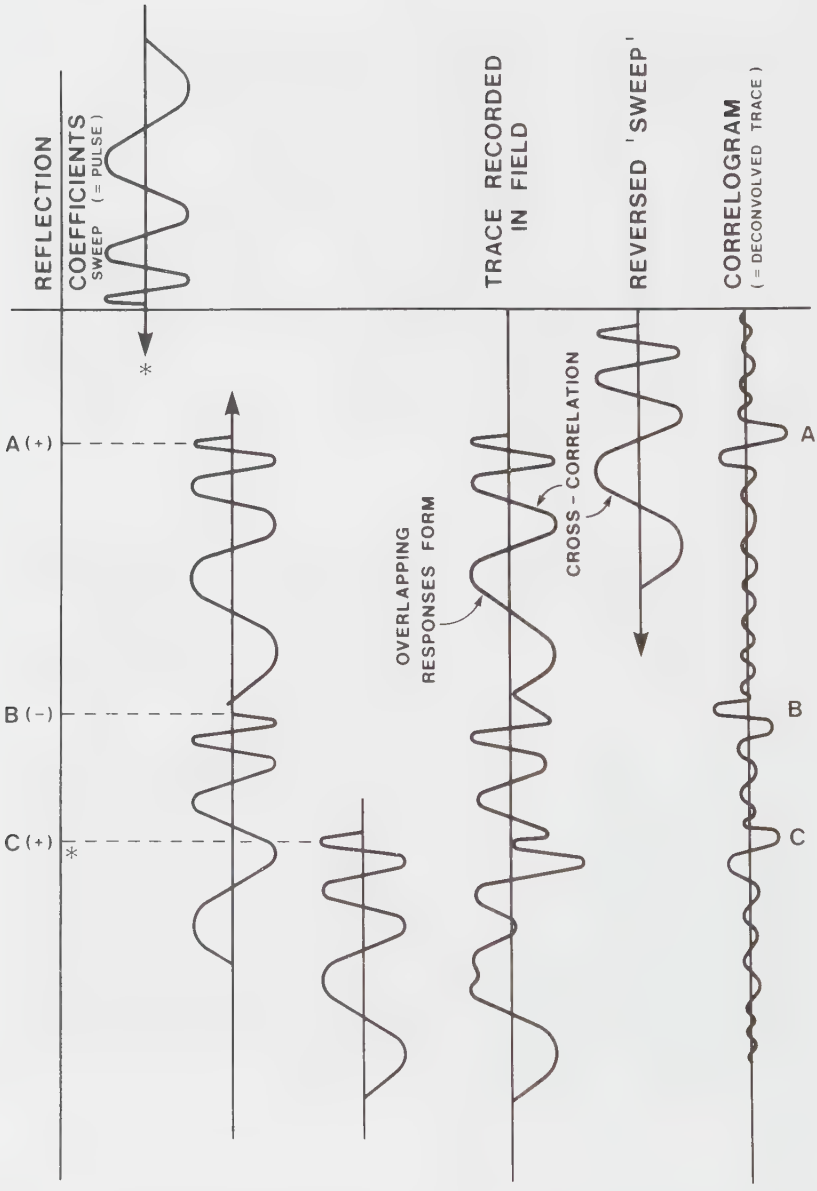


FIG. 9. The deconvolution of a Vibroseis (TM) trace.

sort of data. The techniques used are based on the identification of reflections as occurring beneath a small area on the ground (a 'bin' or a 'cell') rather than at a common depth–point. All traces relating to reflection points within a cell are gathered and stacked in the usual way. Where a traverse line bends, the line of best fit through the cells will lie on the concave side of the bend, and the fold of cover will vary irregularly from gather to gather. Final sections are produced either along the curving best fit line or as projections on to a number of straight-line segments, as the client requests.

Attempts have been made to use the lateral scatter of reflection points on both side of very crooked lines to provide some information about the dips across the traverse. However, little use seems to have been made of these techniques, which are now being superseded by more comprehensive three-dimensional approaches.

3D surveys

A common pattern of exploration in a new area is for a number of broadly spaced reconnaissance lines to be shot in a first year, to be followed in subsequent years by intervening lines if the initial results are sufficiently promising. Normally a rectilinear grid pattern is used so that reflectors identified on neighbouring lines can be 'tied' together by tracing them along the cross lines. As the spacing between lines gets smaller, correlation of events becomes less difficult and the importance of the tie lines decreases. Eventually the spacing may become so small that seismic sections can be constructed at right-angles to the original line direction simply by selecting one CDP gather from each line. A survey for which this is possible is known as a 3D survey and can be treated in new ways. Artificial sections can be constructed at angles to the original lines. It is also possible to show variations in seismic amplitude at a given reflection time over the entire area. Such sections ('horizontal slices') have some of the properties of contour maps, and can be especially useful in tracing sinuous, low-amplitude features such as former river channels and sand bars. Where an unconformity or other important surface has a generally flat dip, it is possible to display amplitudes along the dipping plane if this seems desirable. It also becomes possible to migrate seismic events from dipping interfaces or diffracting points in three dimensions so that the true locations of the reflections can be identified.

The main disadvantage of 3D surveys is, of course, their cost. Although there are some savings to be made in surveys planned to be 3D from the outset by discarding the tie-lines needed in less detailed work, the vast amount of data is costly to acquire and costly to process. A 100 km^2 survey might involve the acquisition of 1000 line-km of data at 100-m CDP spacings. If a 96-channel system were being used with sampling at 0.002 s intervals for a four-second record length, 2000 million individual data items would be recorded, reducing to 40 million after 48-fold stacking. This would form a single three-dimensional array of values from which an enormous amount of information could be extracted by sophisticated processing. Such surveys seem to be economically feasible at present only where field development rather than pure exploration is involved. Under these circumstances, the cost, often estimated as equivalent to

one or two wells, can be justified by the savings in drilling and by the optimization of hydrocarbon recovery.

3D surveys are attempted on land even less often than at sea since acquisition costs are much greater onshore than offshore. The techniques used may also differ, with large numbers of groups of geophones being laid out over an area through which the sources are moved along a relatively small number of traverse lines. CDPs are thus located not merely beneath the lines of traverse, but also at many points offset from them. A completely different set of acquisition and processing problems arise.

Interpretation of Seismic Sections

The idea that reflections are associated with bedding planes is fundamental to all seismic interpretation. Reflections may also be associated with lithological boundaries where these coincide with bedding surfaces, but where rock types change laterally the reflections have a strong tendency to follow the bedding planes rather than the lithological boundaries. Hence a reflection can be thought of as corresponding to a geological instant, or time-stratigraphic marker, and as such it is a true representation, in reflection time at least, of the structural attitude of a sedimentary stratum.

Structural interpretation

For structural interpretation, prominent or important reflections are correlated across the seismic sections and tied around the loops of the survey. Times are picked and plotted at reference points on separate maps for each of the chosen reflections and the maps are then contoured in time, usually with a contour interval of ten or twenty milliseconds. The result is a suite of time-structure maps which, except where strong lateral velocity changes are present, are closely related to geological structure. Time-isopachs between reflections are often made in order to discover or emphasize subtle geological changes.

Where strong lateral velocity changes are known or thought to be present the time-structure maps are converted to depth maps. This can be accomplished by determining the average velocity to a particular reflection at each map reference point from the NMO, contouring the values to produce a velocity map, and multiplying this by the time-structure map to produce a depth map for the reflector. The procedure can be repeated for each time structure map.

An alternative method is to construct iso-velocity overlays for the seismic sections and convert the time sections to depth sections by means of a computer program. Depths to reflectors can then be read and mapped directly.

Time-structure maps suffice for most areas, but depth conversions are usually made where drilling is contemplated, and always where critical dip is in question.

Stratigraphic interpretation

An assumption necessary for stratigraphic interpretation of seismic sections is that even within rocks which are in the gross sense homogeneous, bedding planes are associated with small reflection coefficients and that the

superposition of the small reflections results in 'line-ups' which are parallel to the bedding or cross-bedding within the gross rock unit. The logical basis for this assumption is not compelling, but the evidence is (Fig. 10). If the proposition is accepted, it is possible to analyse seismic sections in a way which will reveal much about depositional history, palaeo-environments, and facies distribution.

The first step requires a break with traditional seismic interpretation which has always been concerned with following reflections as far as possible in order to map structure. Stratigraphic interpretation begins with identifying the surfaces at which reflections terminate. Such surfaces are referred to as 'sequence boundaries', and represent gaps in the geological record where sediments corresponding to some geological time interval are absent by reason of non-deposition or erosion. They divide the seismic section into a number of 'sequences', each of which corresponds to the sediments deposited during a certain geological time span.

Sequence boundaries are characterized by the termination of reflections in any of the ways illustrated in Figs 10 and 11. Once identified they can be followed across sections and tied around loops in the same way as any other seismic event. 'Reflection' times can be picked for sequence boundaries and they can be mapped in the same manner as reflections. The 'boundary relationships' of the beds above and below the boundary can be recorded and illustrated on the maps by colours or conventions. For the overlying beds the relationship can be parallel, onlapping, or offlapping. For the underlying beds it can be parallel, oblique, sigmoid, or truncated. Maps showing such relationships are valuable in identifying areas of erosion and in determining the direction of sediment transport.

Representative reflections from each of the sequences can also be transferred to a 'chronostratigraphic section' (Fig. 12). The horizontal axis of the chart carries numbers corresponding to the shot-point numbers of the seismic section; the vertical axis represents geological time at no fixed scale. Horizontal lines correspond to geological instants, even though it may not be known precisely what instants. The important point is that every line is later in geological time than the one below it. The selected reflections are represented by horizontal lines whose length and lateral position correspond to the distance over which they can be seen on the seismic section. All structural information is lost in the process. The chronostratigraphic section can be thought of as a two-dimensional stratigraphic column which shows where rocks of a certain geological age are present, where they are absent, and for what reason. It is similar to a faunal distribution chart and forms a useful link between geophysicist and palaeontologist.

Ordinarily the sequences form an alternating series of transgressions and regressions, and the sequence boundaries are the result of changes in relative sea level. Many of the important sea-level changes were world-wide events and sequence boundaries can and have been used to predict the ages of sequences, in the absence of any other geological information. In the correlation of seismic sections which are separated by some distance, sequence boundaries are usually more reliable markers than reflections.

The character and configuration of reflections within a sequence, or, where continuous reflections are absent, the 'grain' of the seismic section, carry

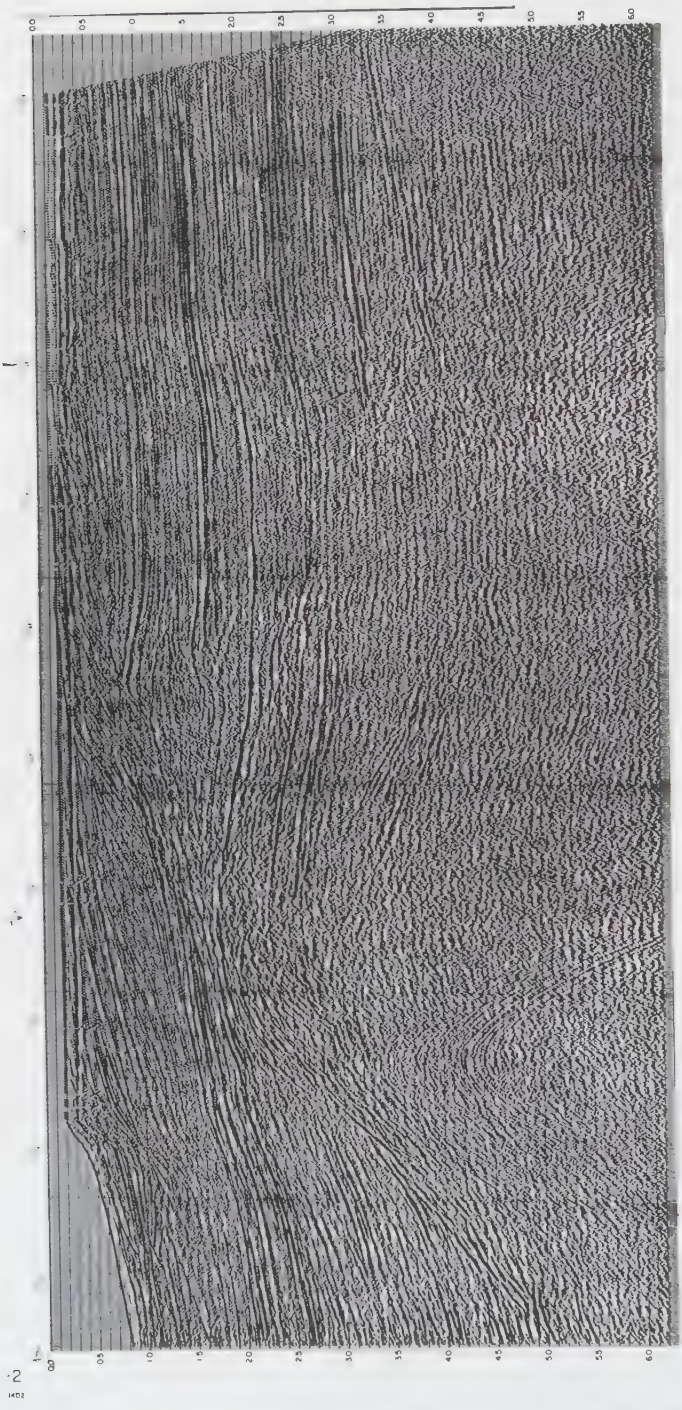


FIG. 10. Example of a seismic reflection cross-section from an offshore survey. (Courtesy of British Petroleum.)

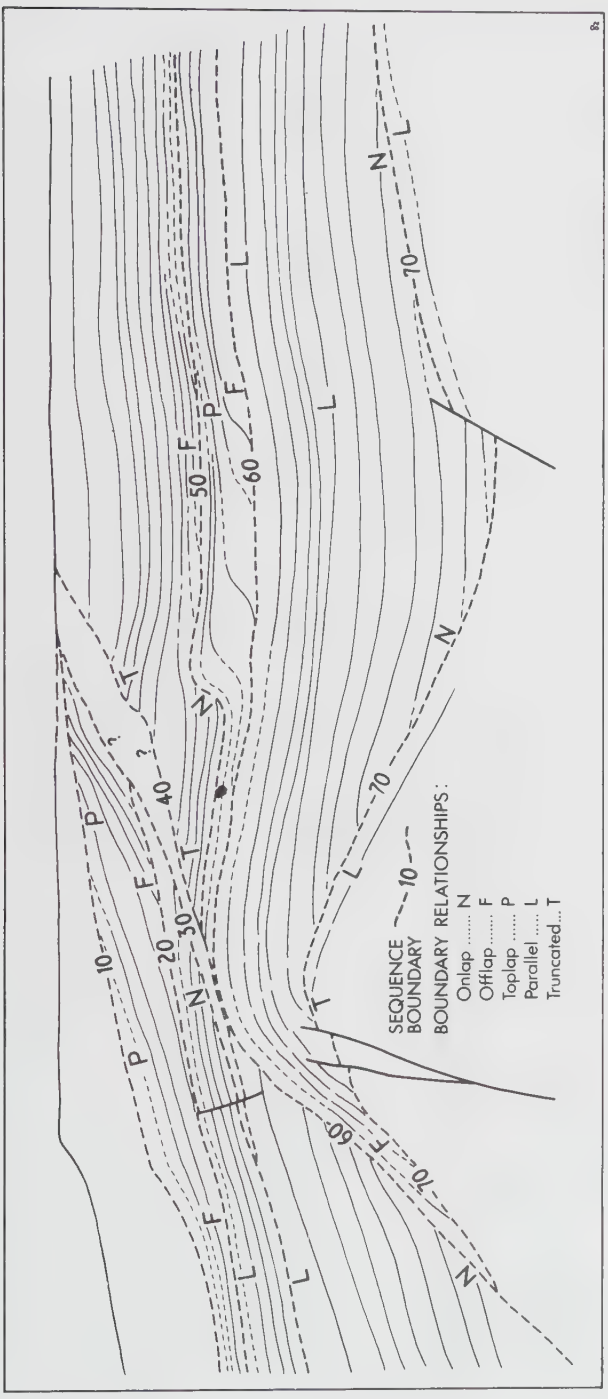


FIG. 11. Interpretation of the section shown in Fig. 10.

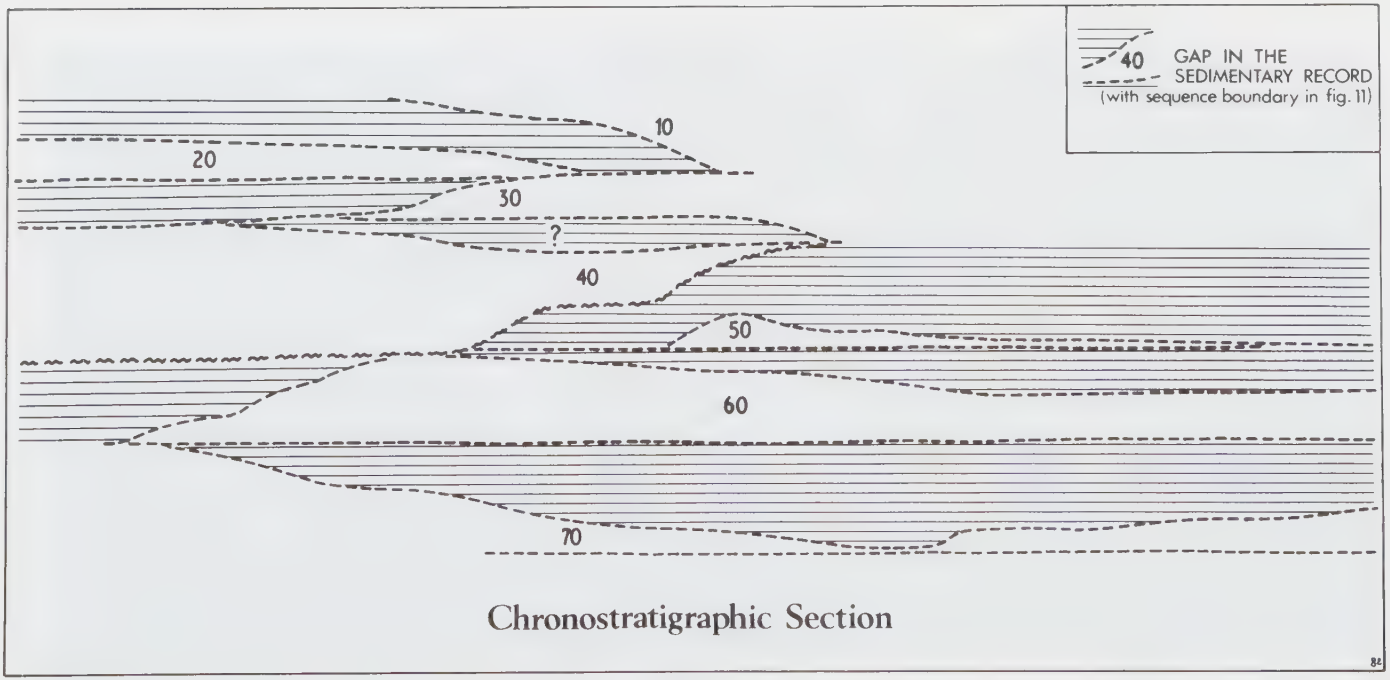


FIG. 12. Chronostratigraphic diagram for the section shown in Fig. 10.

information concerning depositional environment and facies distribution. If, as in Fig. 10, the section crosses an old continental shelf edge, the identification of the shelf, slope, and deep-water environments is simple. Even where all of these elements are not present, or are not obvious, the classification of reflections in terms of abundance, amplitude, continuity, and parallelism or divergence is useful. Displayed by colour or convention on an isopach of the sequence, these classifications are a valuable aid to the interpretation of subsurface data.

Interval velocities can serve as a rough guide to lithology provided that the interval involved is a stratigraphic unit, i.e. a sequence or part of a sequence. Stacking velocities are not suitable for this purpose because they are derived from the NMO of strong reflections. Such reflections usually occur within sequences, and sequence boundaries are often characterized by the lack of a good reflection. Hence interval velocities derived from stacking velocities usually straddle one or more sequence boundaries and are stratigraphically meaningless. It is possible, by the careful analysis of more velocity data than is normally used for stacking purposes, to determine useful interval velocities for sequences. However, as the thickness of the interval decreases the probable error in the calculation increases rapidly, so the method is likely to fail where it is most needed.

Interpretation of Seismic Traces

The magnitudes and signs of reflection coefficients affect the amplitudes and polarities of the received signals, and modern recording techniques now permit these 'true amplitudes' to be recovered. It is therefore theoretically possible to determine the reflection coefficients from the seismic signal and furthermore, if the details of a complete series of reflection coefficients are known, the acoustic impedances of the corresponding rock units can be calculated. An initial (near-surface) velocity is the only other information needed. It follows that the individual seismic trace, as distinct from the seismic section, contains useful information. Methods have been developed to display such parameters as reflection amplitude and frequency on seismic sections, but they have not yet been widely accepted. A more promising technique appears to be the inversion of a seismic trace into an approximation of a continuous velocity log.

The most obvious obstacle to such an inversion is the presence of noise, since clearly not every event on a seismic trace corresponds to a reflection from an appropriately located interface. Furthermore, some velocity changes, notably the gradual ones due to increasing compaction of sediments with age and depth, do not produce identifiable reflections. These slow variations must be determined from NMO data in areas without subsurface control, and from well-shoot or continuous velocity logs where holes are available. Initial velocities can also be determined from the same sources.

The fact that reflection coefficients depend on densities as well as on velocities presents another, although less serious, difficulty. In some presentations no attempt is made to convert to velocities and the result of the inversion process is simply termed an 'acoustic impedance log'. In others the reflection equation is transformed into one involving velocities only, by use of

one of a number of experimentally determined relationships between velocity and density.

The use of velocities estimated from reflection amplitudes in exploration lies very close to the present limits of the practicable, and satisfactory results are being obtained mainly where the geology is well understood and where there is already abundant subsurface information. It is significant that the method was first developed and is most intensively used in Western Canada, largely to locate porous zones in Palaeozoic carbonates. It may become more widely applied as seismic data quality continues to improve.

Of the several possible objectives of analysis of single seismic traces, the most success has probably been achieved in interpreting thin beds. The problem of locating a thin reservoir bed or estimating its thickness is a familiar one in both exploration and field delineation. Where a bed is known to exist in one borehole and is absent in another nearby, the position and nature of its termination can be investigated by studying subtle reflection changes in the zone of interest. A seismic model can be prepared using the general form of the seismic section in the area and the detailed geological logs of the two holes, and a synthetic seismic section can be generated which includes the bed termination. After a few trials a model is usually obtained which matches the actual seismic section and therefore represents a possible solution. If sufficient control is available, it may be a unique solution.

The method, which involves converting a geological model into reflection coefficients and convolving these with the seismic pulse for a number of traces, sounds tedious, but if done using a computer with an interactive graphics terminal, it is rapid and not expensive. The same techniques can be applied to the investigation of suspected direct indications of hydrocarbons.

Direct Indications of Hydrocarbons

Direct indications of hydrocarbons depend on the fact that the velocity of a porous rock is affected by the fluid which it contains. Since seismic waves travel appreciably slower in hydrocarbons, particularly gases, than in water, it follows that replacement of water by hydrocarbon will change the reflection coefficients at the boundaries of the porous unit and that reflections will be generated from fluid interfaces within the porous rock.

The seismic interpreter has only the form and amplitude of the reflections to work with, and analysis for direct indications essentially involves study of the magnitude and sign of the reflection coefficients associated with the suspected oil or gas accumulation. True amplitude recovery, which has the objective of presenting the reflections in such a way that their amplitudes are proportional to the relevant reflection coefficients, is thus almost essential.

Direct indications were first noticed in areas where poorly consolidated sandstone reservoirs had velocities lower than the overlying shale, even when water-filled. This resulted in a negative reflection coefficient at the top of the reservoir. Where gas was present, the density and velocity of the sandstone were reduced, increasing the magnitude of the coefficient, and the amplitude of the resulting reflection. The effect was noticeable even on routinely processed sections, and was named a 'bright spot'. For a short time there was thought to be a simple correlation between bright spots and gas accumulations, but it was

soon realized that direct indications can take a variety of forms. Depending on the relative acoustic impedances of the reservoir and the overlying rock, the presence of free gas may be indicated by the strengthening or weakening of a reflection, by its appearance or disappearance, by a change of its polarity, or by a combination of these effects.

A positive reflection coefficient is always present at the gas/fluid interface in a reservoir, in some cases generating a horizontal reflection known as a 'flat spot'. If the gas accumulation is sufficiently thick the effect of its low velocity may cause the flat spot to sag slightly in the middle.

Gas accumulations also absorb the higher frequencies strongly and as a result reflections from below a gas reservoir may be noticeably weaker and of lower frequency than elsewhere.

None of the above effects are in themselves proof that gas is present in a structure, but where several occur together the probability is that there is some free gas.

There are a number of limitations on the use of the method, the first being that fairly high porosity in the reservoir is necessary if reflection coefficients are to be altered to the required extent. Sandstones at depths greater than about ten thousand feet and carbonate reservoirs at any depth seldom have such porosity.

Secondly, the difference in velocity and density between water and oil is slight, and it is the presence of free gas which generates the seismic effects. Unfortunately a small amount of gas has the same effect as a large amount, and many legitimate direct indications can be seen on structures which produce only gassy water on test.

Finally, the presence of gas is only one of a great many things which may cause amplitude and phase changes in reflections.

SEISMIC REFRACTION

When a seismic wave encounteres a boundary at which there is a change in acoustic impedance, some of the energy is reflected while the remainder passes through and is refracted. The wavefront approach to refraction is complicated and the uses of refraction are most simply understood from ray-path approximations.

A seismic ray striking an interface at anything other than a right-angle and passing through it, continues on its way at a different angle. Downward ray paths become steeper after passing across interfaces where velocity decreases, but will flatten out in the more usual cases, shown in Fig. 13, where there is an increase in velocity with depth. For one particular angle of incidence on each such interface this flattening will reach the point at which the refracted ray will travel along the interface. At greater angles of incidence the seismic energy is totally reflected, since there can be no refracted ray. The critically refracted ray travels with the velocity appropriate to the lower, faster medium, and while doing so re-radiates energy upwards into the lower velocity layer at the angle of critical incidence. These returns can be detected at the surface, and a form of hare and tortoise race can be imagined between various rays. If only the direct ray and the ray along the first refractor in Fig. 13 are considered, it is fairly obvious that the direct ray will arrive first at the nearer geophones, but that at

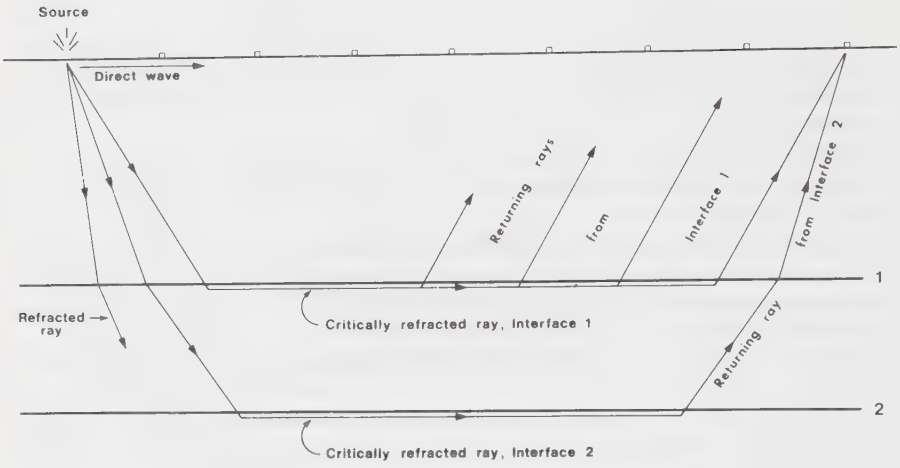


FIG. 13. Principle of the seismic refraction method.

greater distances the disadvantage the refracted ray suffers in following a longer path is outweighed by the fact that much of this path is travelled at a higher velocity. However, there is also competition between the two refracted rays shown, and it is by no means certain that the first refracted ray will have overtaken the direct ray before it in turn is overtaken by the second.

In reflection work, a near-surface refraction is merely regarded as an annoying form of shot-generated noise which, because of its comparatively low velocity, persists at the furthest geophone until inconveniently late in the seismic record. It is, however, possible to make use of refraction directly in exploration, and refraction surveys of deep sedimentary structures have considerable historical importance. The limitations of the method can be easily appreciated; it relies on velocity always increasing with depth at interfaces which are relatively few in number and at which there are large changes of velocity. Small changes and multiple interfaces will result in a large number of overlapping weak arrivals which will be almost impossible to interpret. Although refraction surveys are still occasionally used to investigate thick sediment accumulations, their commonest applications are in investigations of the deep crust and upper mantle, and of the shallow layers of very low seismic velocity produced by weathering and by recent sedimentation. Crustal studies lie beyond the scope of a discussion of oil exploration methods, but the determination of the static corrections required to correct reflection data for the effect of the near-surface low-velocity layer (LVL) is of considerable importance.

The need for static corrections has already been discussed, but without considering in detail how the necessary depths and velocities might be obtained. Where refraction is used, the equipment and field techniques differ markedly from those used for reflection work.

Only twelve, or, less commonly, twenty-four, recording channels are used and each channel is connected to only one geophone. This is acceptable because interpretation is rarely based on timing more than the first arrival of source energy and complicated arrays designed to suppress noise are not necessary.

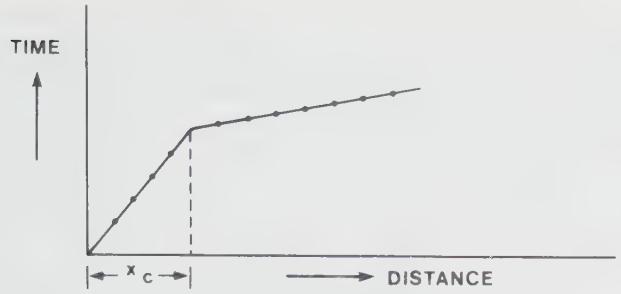


Fig. 14. Refraction time–distance plot for a two-layer case.

Indeed, the arrivals to be observed are among those that conventional geophone arrays are designed to attenuate. Digital recording is also not common; although modern 'enhancement' seismographs sample the incoming signal digitally, and store the digital values in temporary memories so that the results of repetitions can be added together instantly, the final permanent record is normally produced as a single paper copy only.

The length of a refraction spread depends on the thickness of the low-velocity layer, since the primary requirement is that arrivals from the base of that layer should be recorded on at least half the geophones. Lengths of one or two hundred metres are common and small explosive charges, of the order of a few ounces, and weights of a few hundredweights dropped from heights of a few metres are sufficient over such distances. Weight dropping is particularly suitable with enhancement instruments, since it allows quick repetition and summation, with corresponding improvement in signal-to-noise ratio.

Interpretation of refraction spreads is based on the time–distance plot, a simple example of which, with only a single interface separating two layers, is shown in Fig. 14. The velocity of the direct wave in the overburden is given by the gradient of the first straight-line section and the velocity along the refractor is given by the gradient of the second. The depth to the refractor can be calculated from the interceptor of this second line, as extended backwards, on the time axis, i.e. at zero distance. The refractor dip will change the gradient, and therefore the apparent velocity, increasing the latter if the ray is travelling up-dip and so being brought closer to the surface at greater distances, and decreasing it if the ray travels down-dip. Results must be obtained with the source at each end of the spread in turn, so that a true velocity can be calculated from the two apparent velocities.

Quite apart from the difficulty of identifying the actual instant of energy arrival, there are several problems in interpretation. If velocity decreases with depth anywhere within the overburden, or if the refracting layer or ground surface is very irregular, or if there are numerous interfaces above the bedrock surface, simple interpretation methods will no longer work, and it may even be that no accurate interpretation is possible. In engineering site investigations, where refraction methods are also used, some of the difficulties are overcome by obtaining additional results with the source in line with the spread but offset some distance from the nearest geophone. These techniques might with advantage be applied to oil exploration LVL studies, where they are now seldom used.

MAGNETICS

Aeromagnetic surveys are the quickest, and in most areas the cheapest, form of geophysics which can provide useful exploration information. The basis of the method is that certain minerals, of which magnetite is by far the commonest and most important, produce easily detectable 'anomalies' in the magnetic field. Since magnetite is a very minor constituent of sedimentary rocks, an aeromagnetic map can be used to estimate the depth to the basement beneath the sediments. Even where sediments do contain magnetite, they produce only negligible magnetic fields at an airborne sensor, partly because the effects of thin, flat-lying sources decrease rapidly with height and partly because the fields from randomly oriented magnetite grains tend partially to cancel each other. Sediments can, however, influence a ground magnetometer, as can the small pieces of iron scrap which are abundant in populated areas. For these reasons, and also because ground measurements are very slow if large areas are to be covered, the work is almost always done from the air.

The Earth's Magnetic Field

Anomalous magnetic fields due to geological sources are measured against the background of the earth's magnetic field. All magnetic fields are essentially bipolar in nature, i.e. they can be regarded as caused by sources which consist of two poles of equal strength and opposite sign, separated by a small distance. In the limit, when this separation becomes vanishingly small, the source is described as a magnetic dipole. The magnetic field of the earth approximates to that of a dipole located at its centre and inclined at about 10° to its spin axis. Field strength is measured in nano Tesla (nT), more commonly known to geophysicists as 'gammas'. At the earth's magnetic poles the field is about 60 000 nT and vertical, whereas at the equator it is about 30 000 nT and horizontal. It is caused by electric currents circulating in the earth's core, and changes slowly over the years in both magnitude and direction. These variations must be taken into account when comparing surveys flown more than a few months apart; together with variations with latitude and longitude, they are described by a complicated experimentally-determined formula known as the International Geomagnetic Reference Field (IGRF). The IGRF generally is a reasonable approximation to the regional field in well-surveyed areas where the control on its formulation was good, but may be unsatisfactory in remote regions.

Apart from the long-term changes described by the IGRF, there are daily cyclical changes (diurnal changes) due to fluctuations in the electrical currents in the earth's ionosphere. The daily amplitude is normally of the order of 20 nT, which means that careful corrections must be applied to airborne measurements which are typically made to a precision of 1 nT and contoured at intervals of 5 nT. During periods of sunspot activity, streams of high-energy protons from the sun strike the upper atmosphere and enormously increase the ionospheric currents, causing changes of sometimes hundreds of nT over times as short as twenty minutes. Such magnetic 'storms' (which are unrelated to meteorological or electrical storms and may occur on days when the weather is fine and clear) cannot be satisfactorily corrected for, and work must be

abandoned until they are over. During a survey, diurnal changes are monitored by a fixed ground magnetometer which provides a permanent record on chart or magnetic tape. Corrections are made using this record directly, or by adjustment on a system of 'tie-lines' at right-angles to the main lines of the survey, or by a combination of the two. In recent years it has become increasingly common for the spacing between the ties to be reduced to only two or three times the spacing between the main lines; not only does this improve the diurnal control but the accuracy of the final contours is less dependent on the initial choice of flight-line direction.

The magnetic anomalies due to the natural magnetism of rocks are superimposed on the earth's main field and its daily variation. Since magnetite loses its magnetic properties at about 600 °C, a temperature reached in the lower part of the continental crust, local features on aeromagnetic maps must all be of upper crustal origin. Anomalies over thick sediment piles are only of the order of a few nT in amplitude, but in areas of exposed basement changes of hundreds and even thousands of nT are commonplace. The largest anomalies known reach to positive and negative values of more than 150 000 nT, several times the strength of the earth's normal field.

Airborne Instruments

Aeromagnetic measurements are usually made with either a fluxgate or a proton precessing magnetometer. The fluxgate is the older of the two, having been developed during the Second World War for detecting submarines. It relies on the saturation magnetization of bars of soft iron in strong magnetic fields. Since the properties of all components involved in obtaining a magnetic field estimate from the saturation phenomenon are very temperature-dependent, the instrument reading will change with temperature even if the sensor is kept in a constant field. This 'drift' has to be removed, together with the daily field variations, before a usable magnetic map can be produced. The fluxgate measures only changes in magnetic field and not the absolute field strength, but does provide a continuous record of those changes. It is not suitable for mounting outboard of an aircraft, and so must be artificially isolated from the aircraft's magnetic field by a system of compensating coils and magnets.

The other common, and now the commonest, form of airborne instrument is the proton precession magnetometer. Protons (i.e. hydrogen nuclei) can be made to gyrate or precess in a magnetic field, and in so doing will emit a radio wave with a frequency proportional to the field strength. This frequency can be measured and converted into an absolute magnetic field value. The instrument has the enormous advantage of measuring total field automatically, whereas the fluxgate requires an elaborate orientation system. A proton sensor can therefore be placed in a 'bird' towed well away from the aircraft's magnetic influence or in a relatively light nose cone or tail boom. The main disadvantage is that readings are made discontinuously and precision is adversely affected by shortening the reading cycle. Most modern systems read once every second, during which time the aircraft will have moved 50 m or more; the actual reading is averaged over about a tenth of this time.

In recent years a third type of instrument, the alkali-vapour magnetometer,

which uses the magnetic properties of electrons rather than protons, has been developed. Since the electron is about two thousand times more magnetic than the proton, alkali-vapour magnetometers typically have sensitivities of 0.01 nT. In fact, little use has been found for this increased precision, one problem being that corrections for diurnal effects cannot be made accurately enough. Surveys have been flown using two alkali-vapour sensors separated vertically by about 60 m, to obtain maps of vertical gradient directly by subtraction, automatically eliminating the diurnal background. Gradient maps, used in addition to the total field maps acquired at the same time, have some advantages in the enhancement of local anomalies and in the suppression of broad regional effects, but it is not yet widely accepted that these advantages justify the considerable increases in cost.

Production of Magnetic Maps

Before an aeromagnetic map can be produced, the aircraft's path must be 'recovered' and related to the magnetic field readings. Survey navigation may be either visual, from maps, photographs, or photo-mosaics, or may use an instrumental system. The latter is, of course, essential over the sea and may be almost so in desert or jungle-covered areas. The Doppler system, in which high-frequency radio waves are beamed downwards from the aircraft, is one of the most commonly used. The change in frequency of the scattered wave which returns to the aircraft is proportional to the velocity over the ground. Doppler systems have the great advantage of not requiring ground transmitting 'beacons', which are usually expensive to install and re-supply, but can only be as good as the magnetic compass which is used as a heading reference. They are also subject to an error when used over the sea because of movement of the sea surface, so fixed radio navigation beacons are usually preferred offshore. A more recent development is the use of gyroscope-based inertial guidance systems in survey work. Again, there is the advantage of having a self-contained system in the aircraft, but inertial navigators with an acceptable level of accuracy are rather bulky and very expensive.

Wherever possible a continuous record of the ground beneath the aircraft is obtained from a vertically mounted cine-camera with a wide-angle lens. Flight path is recovered from this film on to maps or photographs, using the navigation system records, if any, for interpolation. The production of the final maps, which involves integrating the flight path information with a vast number of individual magnetic readings, is a time-consuming and error-prone process. Some improvements have been made by digital processing, but baselining errors due to instrumental and simple plotting errors persist. A surprising number of final maps submitted to clients and even published by government agencies contain such errors, seen as 'herring-bone' shifts of contour line position with flight line direction or as sudden geologically inexplicable changes of contour strike. Any aeromagnetic map has to be looked at with suspicion, and all should show the positions of flight lines and plotted points. The latter information is important not only in the diagnosis of actual errors but also in separating geophysical fact from draughtsman's fancy.

Magnetic coverage to contour map stage can currently be obtained for about $20 per line-kilometre in areas where there are no major operational

difficulties, but if fuel has to be positioned by air to remote strips or long flights have to be made from the operational bases to the survey area, costs can rise dramatically.

Interpretation

Interpretation of magnetic maps has to be based on an understanding of the nature of rock magnetism. Rocks may be magnetized both permanently (remanently), most commonly when cooling from high temperatures, or temporarily (inductively) by the existing earth's field. The induced magnetization is aligned in the direction of the present field, while the direction of remanence may be completely different if either the rock position or the field has changed significantly since the magnetization was acquired. Strongly magnetic rocks are usually magnetized both permanently and inductively, and although for simplicity it is often supposed that the remanence is either small or in the same direction as the induced magnetization, this may not be the case. Fortunately, in oil-search magnetic surveys, calculations are usually directed only towards estimating the likely depths of sources, using methods which are rather insensitive to magnetization directions. These methods range from simple 'rules of thumb' applied to slope extents on magnetic anomaly curves, to more comprehensive calculations using detailed model studies. All are ultimately based on the assumption that the 'wavelength' (width) of a magnetic anomaly is related to the depth of its source, with the narrowest magnetic anomalies being due to the shallowest sources. The depths obtained, by whatever method, are plotted on a map and contours are drawn on what is known as 'magnetic basement'. Since many of the magnetic sources are likely to extend up to the unconformity at the base of the sediments and be truncated there, the magnetic basement surface is in many cases a very useful guide to sediment thicknesses.

There are many possible pitfalls. For one thing, although it is true that an anomaly with a certain spatial wavelength cannot be caused by a source below a certain depth, the reverse is not the case: quite broad anomalies can be produced by quite shallow sources. Again, the source might not be truncated at the basement surface, but might be wholly below it at depth. Moreover, even if a source does reach to the unconformity at the base of the sediments, the rocks immediately above may be of no interest to oil exploration. Igneous basement in many parts of the world is covered by thick sediments which are not magnetic but which, usually because they are either too old or too young, are also not prospective. Finally, a certain amount of igneous material within a sedimentary succession does not automatically render those sediments non-prospective. For example, some oil fields lie beneath a surface layer of basalt which produces very intense patterns of magnetic anomaly.

With so many obstacles to success and with an accuracy in depth estimation even in favourable circumstances seldom exceeding 10–20 per cent, it may seem surprising that magnetics are used at all in oil exploration. However, magnetic information can often be very useful. Archaean gneisses outcrop strongly at both the eastern and western margins of the map area in Fig. 15, and consequently it would seem unlikely that a deep sedimentary basin would underlie the shallow sea in between. The aeromagnetic map shows that the

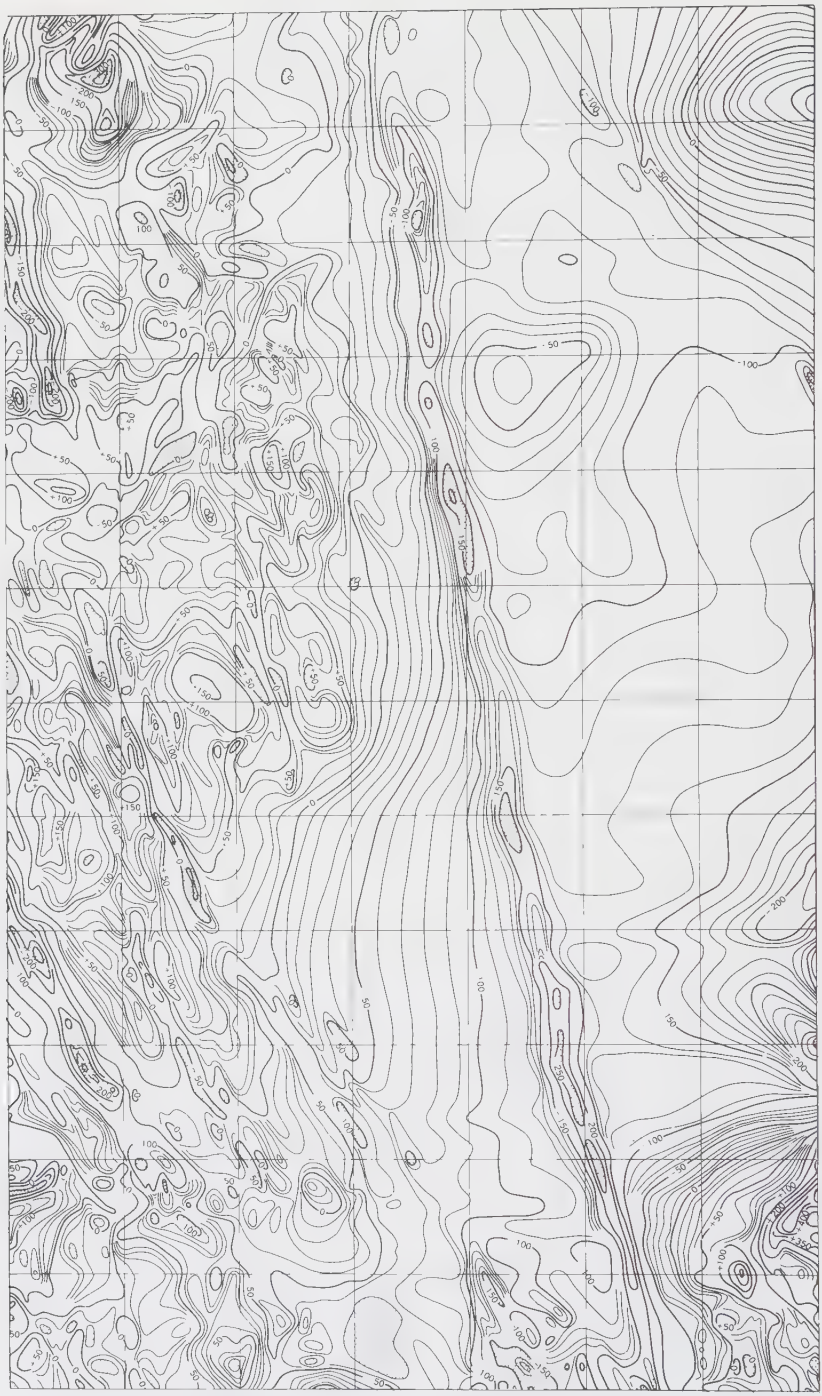


FIG. 15. Aeromagnetic map (square grid of 10-km side). (Copyright Natural Environment Research Council, published with the permission of the Institute of Geophysical Sciences).

Archaean either does not extend beneath the sea or that it has been faulted down to great depths. In either case, thick sediments would be predicted on the basis of the magnetics and their existence has been proven by seismic work. The magnetic map also provides some information which the seismic does not. The long narrow negative anomaly crossing the magnetically 'quiet' area coincides with a rather vague disturbance on the seismic sections which is difficult to interpret. The magnetic pattern is distinctively that of one of the Tertiary dykes common in the region (north-western Scotland).

Filtering Methods

In many cases there is a regional background to a magnetic map which is only partially removed by applying an 'IGRF' correction and which obscures some anomalies of interest. This is generally a serious impediment only if interpretation is being attempted directly on the basis of the magnetic contours and not, as should be done, on the original profile data. The contours are best used simply to obtain correction factors for intersections of flight line and anomaly strike at something other than a right-angle. Nevertheless, a number of methods have been proposed, and are in use either for determining and then eliminating the regional background, or for increasing the contrast between background and the local anomalies.

The commonest method of determining the regional field is to define the gently curving surface (low-order polynomial) which best fits the field data. Alternatively, the field existing on some plane higher than, but parallel to, the plane of measurement may be calculated. In this 'upward continued' field, broad anomalies will be little altered, but narrow anomalies due to near-surface sources will be attenuated and smoothed into the background.

Local anomalies can also be emphasized directly by 'downward continuation' or by calculation of second vertical derivatives. These operations have to be carefully controlled, since they will enthusiastically amplify errors as well as real local features. Traditionally, derivatives or continuation values have been calculated from values read off magnetic contour maps on a circular graticule system. This technique was also used in the construction of 'reduction-to-pole' and 'pseudo-gravity' maps, whose purpose was to reduce difficulties caused by the bipolar nature of the magnetic field. Because of bipolarity, a magnetic source will not lie directly beneath the corresponding anomaly's positive peak, but somewhere between the main positive and the main negative, unless both the earth's field and the source magnetization are vertical. Reduction to pole produces the map that would be obtained over the same geology at the magnetic pole, where fields are vertical; the pseudo-gravity operator goes one stage further and eliminates the negatives which at the pole should flank each positive peak. Both methods need to assume that the magnetic vectors are parallel in all rocks in the area considered, and there will be errors to the extent that this is not so. Since the effect of the errors will be greater the further the area lies from the magnetic pole, it is fair to say that while the conversions work well near the pole, where they are not particularly useful, they do not work well near the equator, where they would be useful.

All the above operators are essentially filters which can be used because the anomalies on a magnetic map can be treated as waves (in space instead of

time), with frequencies measured in cycles per metre instead of cycles per second. The techniques of Fourier analysis can be applied in the same way as to any other waveform. The graticule methods were popular before digital computers were available to carry out Fourier transforms, and the second vertical derivative in particular was used not because of any great theoretical significance, but because it has a particularly simple mathematical formulation. Any desired combination of high-pass and low-pass filters can now be applied to magnetic maps using standard digital techniques, and less direct methods are becoming of historical interest only.

Another possibility with transformation to the frequency domain is the estimation of depth to magnetic basement directly from the frequency spectrum of the magnetic field. This method, which relies on the fact that narrow anomalies are due to shallow sources, can work only if anomalies are plentiful. Generally this will be the case only if magnetic basement is less than 1000 m below the sensor.

Palaeomagnetism

The permanent magnetization of rocks has been studied intensively during the last three decades and the theory of plate-tectonics owes much to an understanding of the record of reversals of the earth's magnetic field preserved in the basaltic floors of the deep oceans. Although the science of palaeomagnetism (the reconstruction of crustal movements from the directions of rock remanent magnetizations) has little direct application in oil exploration, its indirect influence in generating new approaches to the science of geology has been considerable and may be expected to increase.

GRAVITY

The gravity method resembles the magnetic in its reliance upon measurements of a naturally existing potential (inverse square law) field. However, there are many differences in detail and in the problems encountered. In general, the processes which must be gone through before useful field values are determined are more complicated in gravity than in magnetics, but the map making and interpretation are rather simpler.

The Earth's Field

Gravity anomalies are produced by any variations in rock density, since gravity fields are directly proportional to masses. For uniform spherical bodies, and only for such bodies, the gravity field is identical with that which would be produced were the entire mass concentrated at the centre. Since the earth is very nearly spherical and its density can almost be said to vary only with distance from the centre, the spherical field is a good approximation to the earth's actual one. However, the slight flattening at the poles places an observer there slightly closer to the earth's centre than one at the equator and makes him weigh up to a pound more. Also the rotation of the earth exerts on the observer and his gravity meter a centrifugal force which is opposed to the earth's main

field and which reduces it most at the equator. These two effects result in a regional variation in sea-level gravity described by the 1967 International Gravity Formula:

$$g = 978\,031.85(1 + 0.005\,278\,895 \sin^2 L + 0.000\,023\,452 \sin^4 L)$$

where L is the latitude. The units in this equation are milligals, the most commonly used units of gravity field. Some recent maps have values posted in 'gravity units', equal to a tenth of a milligal. Since $\sin 90° = 1$ and $\sin 0° = 0$, the equation implies that the 'normal' gravity at the equator is about 5000 mgal less than at the poles. The rate at which this regional field changes is also variable, being actually zero at both poles and equator and a maximum at 45°, where a 1 km change in latitude produces a change of 0.8 mgal in normal gravity. The 1967 formula replaced an earlier, 1930, formula with slightly different values for the constants. The change was brought about by improvements in absolute determinations of gravity using pendulums or falling weights, establishment of a more comprehensive system of international gravity ties using relative pendulums and geodetic gravity meters, and observations from satellites of the shape of the earth.

Gravity Meters

Gravity surveys on land are now virtually always carried out using spring-balance type meters which are sensitive to gravity changes of as little as one hundredth of a milligal (one part in ten million of the earth's field). Specially adapted instruments are available with ten times this sensitivity. Careful design and construction of the spring system are necessary to bring it close to the point of instability so that a very small change in gravitational force produces a large change in equilibrium position. There are two main types of meter in use; those of one group, represented by the Worden, use spring systems weighing only a few milligrams made entirely of fused quartz, enclosed in an evacuated chamber to reduce temperature effects. LaCoste meters use a steel spring system which, because steel is an excellent heat conductor, has to be kept at a constant temperature by an electrical thermostat. The quartz meters have the advantage of not needing heavy batteries since their rate of heat loss is so small that ordinary dry cells provide sufficient power. However, they tend to be more difficult to read, have higher drifts and, since the spring system cannot be clamped during transit, are easily damaged. The steel meters' reliance on a thermostatted enclosure instead of near-perfect insulation means that a number of improvements are possible. A clamp can be introduced, drift rates are considerably lessened and readings can be taken at any point on the earth's surface by a single setting of a very long calibrated screw. Quartz meters all have quite limited ranges, of the order of 60–200 mgal without resetting, and this imposes some constraints on survey operations. With both types of instrument, drift rates are so low and accuracies so high that corrections must be made for gravity variations produced by changes in the positions of the sun and moon relative to the earth. Fortunately, the 'earth tide' effects can be precisely calculated and removed from the readings before any other operations are performed. Experienced observers can make accurate readings with meters of either type in less than a minute.

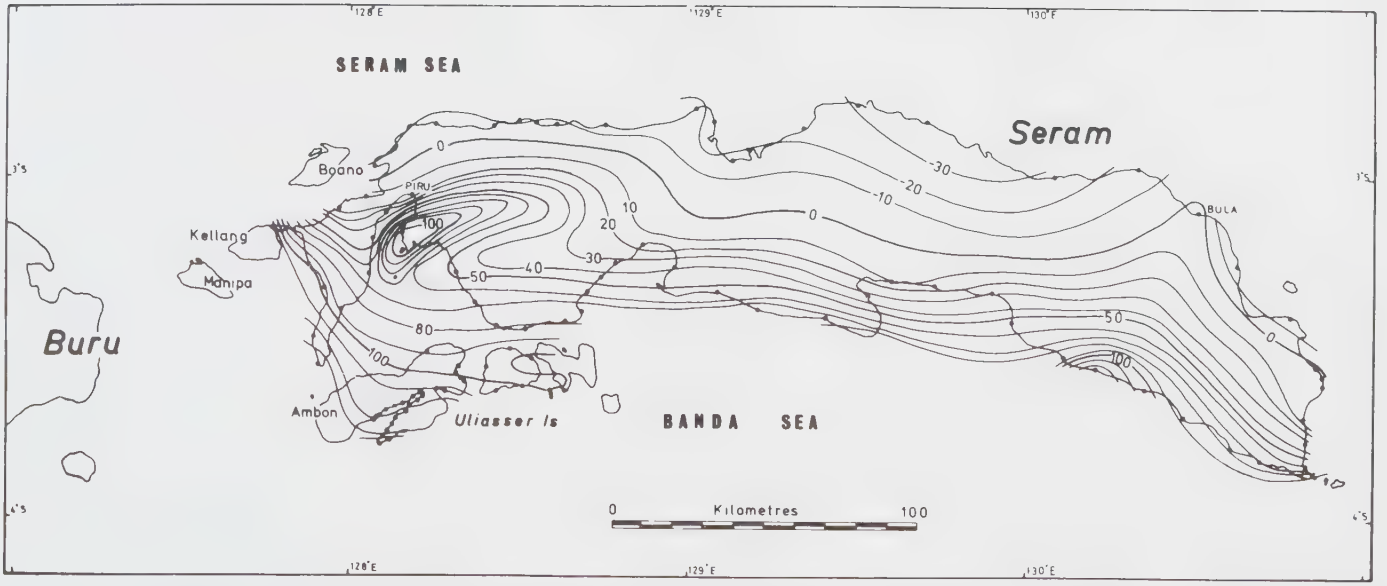


FIG. 16. Gravity map. Reconnaissance Bouguer anomaly map of Seram, eastern Indonesia. Contour interval 10 mgal. The north coast sedimentary basins east and west of Bula are indicated by the gravity lows along the coast. Oil is produced from near the basin margins at Bula. The gravity high south of Piru is due to the presence of dense mafic and ultramafic igneous rocks.

The International Gravity System

Gravity meters measure only differences in gravity between observation points, and in order to apply the 1967 gravity formula to correct for latitude effects, absolute values must be obtained; although surveys can be made using local corrections and arbitrary local base values, useful information is lost by so doing, and it is difficult to compare the results with those obtained in nearby areas. The 1967 formula is compatible with a world-wide system of absolute bases known as IGSN71. IGSN71 bases have been established in most countries and many national base networks are tied to them, relating much of the world's gravity cover to a single datum. Details of IGSN71 stations in any country can be obtained from the Bureau Gravimetrique in Toulouse.

Gravity Reductions

When a meter reading has been converted to milligals, corrected for drift and earth-tide effects and related to the IGSN71, a quantity called the observed gravity is obtained. From this the normal gravity may be subtracted, leaving a value whose difference from zero is due to a number of factors, chief of which is likely to be the height of the point of observation above sea level. This 'free-air' effect which exists because raising the gravity meter above sea level moves it further from the centre of the earth, has a value of about 0.3 mgal/m. After correction has been made for free-air effect and normal gravity the remaining quantity is termed the free-air anomaly.

If, as is usual, the readings above sea level are made at the surface of the earth, there is a mass of rock lying between the observation point and sea level which must also be allowed for. Not only should the rock density be known, but also the shape of the mass distribution. A simple approximation was suggested by Bouguer in the nineteenth century; he pointed out that if the terrain around the reading point was reasonably flat, the effect of the rocks above sea level would be roughly equal to the effect of an infinite, uniform flat plate of the same density and height. The 'Bouguer effect' is equal to about 0.1 mgal/m, varying slightly with density, and, since it acts in the opposite direction to the free-air effect, results in a combined elevation correction of about 0.2 mgal/m (about one hundredth of a milligal for every 5 cm of height change). Measuring station elevations with enough accuracy to make full use of the accuracy of modern gravity meters is thus extremely difficult, especially in regional work where the stations may be several kilometres apart and be linked by helicopter. Barometric levelling has been widely used for such surveys, but accuracies of better than one or two metres cannot be attained with this technique. Recently inertial navigation systems, giving relative heights to a few tens of centimetres, have come to be used, with primary control on height and position in remote areas from satellite observations. Whatever method is adopted, most of the cost of a survey will lie in obtaining the topographic control rather than in measuring gravity.

Application of the latitude, free-air, and Bouguer corrections to the observed gravity produces a quantity termed the 'Bouguer anomaly'. A reconnaissance Bouguer anomaly map is shown in Fig. 16. In high-precision surveys or in surveys in hilly or mountainous areas a further 'terrain correction' is made to

allow for deviations of the topography from the flat plate. These corrections can be very time-consuming and may be impossible to make accurately. They are, in many cases, the limiting factor in the use of gravity methods for geological interpretation.

Rock Densities

Rock density is obviously an important factor, not only in making elevation corrections but also in interpretation. The range is quite small. Light, unconsolidated materials may have densities below 1.8 gm/cc and some basic igneous rocks and metallic ores have densities above 3.0 gm/cc, but the common range is only from about 2.0 to 2.9 gm/cc (water, of course, has a density of 1 gm/cc). In general, sediments are lighter than igneous rocks, but there are many exceptions. Limestones and dolomites, for example, are denser than almost all granites, and some granites have densities lower than some well-consolidated and indurated clastic sediments. Rock salt, with a density of seldom much more than 2.0 gm/cc, lies at the bottom of the common range, and one of the earliest uses of the gravity method was in the search for salt domes.

Finding the bulk densities of rocks is not easy, since laboratory tests can only be made on samples which have been removed from their natural environment and may be atypical. Two field determination methods exist. In Nettleton's method the bulk density of a hill is determined by finding the value which eliminates the effect of the hill from the gravity map when the elevation corrections are made. This assumes that there is no real associated gravity anomaly, which would not be the case if the hill were the surface expression of a dense igneous plug or limestone bed. The second method is to use a bore-hole gravity meter; unfortunately these are expensive, slow, delicate, and require holes at least 15 cm in diameter.

Interpretation

The effects seen on Bouguer anomaly maps arise from sources at all levels within the earth. In contrast to the magnetic method, there is no depth at which gravity sources cease to exist, although the mantle and the core are much more homogeneous than the crust. One of the principal deep-seated causes of variation in surface gravity is isostasy; a mountain mass effectively floats on a much larger low-density root which extends deep into the dense mantle (or, in some areas of crustal tension, is supported by anomalously hot, and therefore low-density, mantle). The gravity effect of this isostatic compensation can be calculated on the basis of one of a number of different mechanical assumptions. It can then be removed to produce an isostatic anomaly map from which some of the regional variations seen on the Bouguer anomaly map will have been eliminated.

Apart from the search for salt domes, gravity readings are made primarily for reconnaissance, to identify areas in which sedimentary basis may exist and to locate places within basins where structural highs are likely (Fig. 16). It should be noted that although the magnetic and gravity fields are mathematically very similar, the ways in which magnetic and gravity maps are interpreted in oil

exploration are very different. In magnetic maps it is the number, size, and particularly the 'wavelength' of the anomalies which concern the interpreter, whereas it is the actual highs and lows on gravity maps which, it is hoped, can be related to areas of thick and thin sediments, respectively.

The most straightforward approach to gravity interpretation is to prepare a geological model, calculate the corresponding Bouguer anomaly map or profile, and adjust the model until a satisfactory agreement is reached between calculations and field results. The increasing availability of digital computers even in field offices and the publication of equations giving convenient mathematical expressions for the gravity fields of bodies of complicated shape have made this work much easier in recent years. For simplicity much interpretation is done on profiles, the geological bodies being assumed for the purposes of calculation to extend unchanged at right-angles to the profile either to infinity (2-D modelling) or to some predefined strike distance ($2\frac{1}{2}$-D modelling). Full three-dimensional model studies are made only if absolutely necessary because of the absence of any definite strike direction in the gravity pattern. Although the interpretation will be ambiguous, since an infinite number of other mass distributions could produce the same gravity anomalies, intelligent application of geological constraints usually allows a useful picture to be produced. The greatest difficult lies in separating effects due to changes in sediment thickness from those due to changes in basement lithology. In some areas the latter are so large that the gravity method is virtually useless as an exploration tool.

It should be emphasized also that no gravity interpretation can ever be regarded as final. As more information becomes available, so the interpretation can be refined and new insights can be gained into the geology of deeper levels or of areas laterally removed from the control. One common approach in an area where an upper layer of sediments has been well tested and defined, and where interest has been switched to concealed sub-basins, is gravity 'stripping', that is the removal of the effects of known layers and structures to produce a map more directly related to the deep geology.

Stripping operations have some features in common with a whole class of filtering operations performed on gravity and magnetic maps. These include high-pass filtering, sometimes in the form of second vertical derivative or downward continuation operations, which emphasize near-surface anomalies (and data errors) and suppress regional effects, and low-pass filters, which may be formulated as upward continuation operators, which determine regional backgrounds. Filtering methods were at one time very popular, but have now been largely discarded in favour of more direct interpretation methods.

One aspect of the fact that interpretation can and should be revised as new information becomes available, is that it is almost always worthwhile to have gravity measurements made in conjunction with seismic surveys, along the seismic lines. This is a very cheap way of obtaining extra gravity data, since the elevations of seismic shot points are normally measured routinely to an acceptable degree of accuracy. The direct correlation of gravity anomalies and seismic structures in an area will not only assist regional gravity interpretation, but may also greatly aid the seismic interpretation. For example, throws on faults across which correlation is difficult or impossible by normal techniques may be estimated from the gravity change.

Marine Gravity

Gravity surveys have been extended offshore first, by adapting conventional meters so that they can be lowered to the sea bottom and read by remote control, and secondly by developing meters which can be read on moving vessels. The problems are many; not only do all the various accelerations to which a surface ship is subjected affect the meter and have to be removed by filtering the results, but the movement of the ship in an easterly or westerly direction alters the meter's rate of rotation about the earth's spin axis and so changes the centrifugal force experienced. This 'Eötvös effect' is most severe at the equator, where an east or west velocity of 1 km/h produces 4 mgal change in gravity anomaly. The difficulty of measuring the Eötvös effect adequately for an aircraft is one of the main reasons why no effective airborne gravity meter has yet been developed and why such development work is now directed towards airborne gradiometers, in which each of the two sensors needed will be subject to the same Eötvös effect. Gravity work occupies a completely different, and much less important place in exploration offshore than onshore. Because a marine meter has to be mounted in a boat large enough to provide a stable platform, the first gravity work in an offshore area is often carried out together with the first seismic survey and the reconnaissance role is lost. Unfortunately, the accuracy of ± 1 mgal which is all that can currently be achieved with marine meters means that the results are really only usable in a regional way. Furthermore, it is difficult to compensate for the effect of the large density discontinuity between sea water and the underlying rocks.

WELL LOGGING

Although in recent years a number of contractors have begun offering surface electrical surveys which, they claim, will detect hydrocarbons directly, and although resistivity readings have been used to some considerable extent in the Soviet Union to outline deep structure, electrical geophysical methods are predominantly used in the western oil industry only in bore-hole logging. By no means all downhole logs are electrical; downhole gravity meters and acoustic loggers have already been mentioned, while methods which use natural and artificial radio-activity are discussed in this section. None the less, electrical logs were historically the first to be run and are still the most widely used. It has to be appreciated that, because coring, which involves repeated raising and lowering of the entire drill string, is extremely expensive, downhole correlations and interpretations have usually to be based either on rock fragments brought to the surface by the drilling mud or on geophysical methods. To understand how these logs function, it is necessary to understand something of the logging tool's environment, the inside of a bore-hole.

Bore-hole Conditions

In rotary drilling, a heavy mud is pumped into the drillhole to act both as a lubricant and as a control on possible 'blow-outs' of high-pressure fluids from sealed formations. The overpressure in the drilling mud forces it into the pore spaces of the surrounding rock, although most of the solids remain on the hole

walls as a 'mud cake'. The formation water is forced back by the mud filtrate from what is known as 'the invaded zone'. The mud cake will be thickest where the filtrate enters the rock most readily, i.e. where porosity and permeability are greatest. Elsewhere, sediment may be eroded by the circulating mud and cave into the hole, which may therefore be wider in some places and narrower in others than the nominal diameter. Electrical measurements can only be made in such uncased holes.

SP Log

The simplest form of electrical log records downhole changes in natural potential (self-potential or SP) with reference to a fixed electrode at the surface. Variations in SP arise principally because shales are permeable to the positively-charged sodium ions in saline formation waters but not to the larger, negatively-charged chlorine ions. Sodium ions pass directly from sandstone aquifers into adjacent shales and return via the drilling mud. Where, as is usually the case, the mud is less saline than the formation water, a negative SP will be associated with sandstones and a positive one with shales. The SP log, also known because of this feature as the shale log, is thus a valuable correlation tool.

Resistivity Logs

Measurements of resistivity require a minimum of four electrodes, between two of which current is passed while the potential difference between the other two is measured. Large numbers of different arrays and systems are possible, but only a few have become well-established in the industry. Standardization is very important, since unless standard arrays and instruments are used, correlations cannot be made between holes with any degree of confidence.

Although four electrodes are needed, it is not necessary that they all be lowered down the hole on the logging tool, and in the 'normal' log, only one current and one potential electrode are mobile while the others are fixed near the top of the hole, either within it or on the surface. If the two downhole electrodes were surrounded by a uniform homogeneous earth, the resistivity could be calculated from an equation relating current, voltage, and electrode separation.

In practice the surroundings are very far from being uniform and the calculated resistivity is only an apparent one. The smaller the inter-electrode distance x, the greater the effect of the mud and of the invaded zone, and the less the influence of the true formation resistivity. To solve this problem holes are usually logged simultaneously with both short ($x = 16$-in) and long ($x = 64$-in) normal arrays on a single probe or 'sonde'. The resistivities of the invaded zone and the undisturbed formation beyond the zone can then be determined from standard curves, provided that the mud resistivity is known. In interpreting the logs it has to be remembered that high-resistivity beds will appear thinner than they really are and low-resistivity beds will appear thicker, by about the electrode separation distance, and very thin beds will be poorly defined.

Resistivity estimates made using the short and long normal logs can only be approximate since the radius of the invaded zone is not known. The third

necessary parameter is often provided by the lateral log, in which two current-source electrodes are mounted 18 ft 8 in apart on a sonde, with a potential electrode 32 inches from the lower one; the second potential electrode is at the top of the hole. Not surprisingly, this asymmetric arrangement gives rise to asymmetric logging curves. The depth of investigation is sufficiently great that the results are scarcely affected by the mud and invaded zone resistivities. Combination of the normal and lateral logs allows a full interpretation of thick beds, but not of beds less than 18 ft thick.

Knowledge of the resistivities of the formation and the formation water allows porosity to be calculated, and there is also a relationship between permeability and the radius of the invaded zone. The permeability also dictates the thickness of the mud cake, which is directly measured by the microlog. This uses three equally-spaced downhole electrodes, two for potential and one for current, about 2 inches apart, with the remaining current electrode at the top of the hole. The very short spacing means that a spring system must be used to press the electrodes against the side of the hole, and the tool is usually adapted to measure hole diameter at the same time (caliper log). The microlog efficiently detects thin beds and records high resistivities opposite impermeable formations where no mud cake is formed. Three or four microlog electrodes mounted at 120° or 90° intervals around the circumference of a sonde can be used to measure formation dips.

Many other electrical logs have been used, and in recent years there have been moves towards systems such as the laterolog which use more than the minimum four electrodes. The extra electrodes confine and focus the current flow so that greater penetration can be obtained without increasing the electrode spacing and decreasing definition. Focused-array logs have not reached the same degree of acceptance and standardization in the industry as have lateral and normal logs.

All direct-current resistivity work relies on electrical contact being made via the drilling mud, and so is impossible where the mud is oil-based and non-conductive. Induction logs, where conductivity is measured by inducing currents electromagnetically in the formation waters, can be obtained in such holes. Receiver and transmitter coils are mounted at opposite ends of the sonde, and the received field will to some extent depend on the conductivity of the surrounding media. Additional coils may be added to obtain a focusing effect.

Radioactivity Logs

Cased holes can be logged by nuclear methods, and are divided into those which measure the natural radioactivity of the formations penetrated and those which use radiation stimulated by lowering an artificial source into the hole.

Natural radioactivity derives chiefly from uranium, thorium, and potassium, the first two being the starting points for chains of radioactive decay in which new elements are produced which are themselves radioactive. Only about one atom in every ten thousand of potassium is potentially radioactive, but because of the element's great abundance in the upper crust, its contribution to the natural radiation field is of the same order as those of the more active heavy elements. Downhole gamma radiation may be measured

with a simple total-count scintillometer, which counts light flashes recorded when the gamma rays which are emitted during radioactive decay are absorbed in a sodium iodide crystal. Alternatively, the energy level of each light pulse may be recorded by a spectrometer, in which case the relative concentrations of the different radio-elements may be estimated. Radio-elements are preferentially concentrated in certain types of sediment and particularly in black shales, since uranium is 'fixed' in an insoluble form in a reducing environment; hence the 'hot' shales of the North Sea, which are amongst the most important source beds. The main use of the natural gamma log is as a tool for correlation between holes.

If a strong radioactive source is lowered down a hole, many gamma rays will pass through the mud and casing and enter the surrounding rock. There they will collide with electrons in the mineral atoms and a proportion will be scattered back towards a detector in the hole. The degree of back-scattering is proportional to the number of electrons in unit volume of the rock, which is closely related to rock density, since the atomic weight of an atom is roughly equal to twice the number of orbiting electrons. The main use of the gamma-gamma or density log is in estimating porosity, since the lithology of the formation will usually have been identified from the rock cuttings and the densities of the minerals of the matrix will be well known.

Neutron logs also require an artificial source to be lowered into the bore-hole. High-energy 'fast' neutrons lose energy mainly by collision with hydrogen nuclei, eventually being 'thermalized' to energies appropriate to the temperature of the surrounding medium. Thermal neutrons may be captured by certain nuclei, resulting in the emission of gamma rays, or may simply be back-scattered to a neutron detector in the hole. The hydrogen content of the wall rocks may be estimated by measuring either the gamma rays or the neutrons, but in the former case the nature of the capturing nucleus can also be estimated, by measuring the gamma energy. Hydrogen concentration is a measure of porosity, since both water and hydrocarbons contain hydrogen, while an indication of the nature of the pore fluids is provided by the extent to which the characteristic radiation from neutron-capturing chlorine nuclei is detected.

Other Logs

Study of the subsurface thermal regime is assuming increasing importance in oil exploration since thermal conditions control the formation, migration, and degradation of hydrocarbons. However, reliable heat-flow measurements can be made only in a hole which has had time to re-stabilize thermally after the disturbance caused by drilling and particularly by the circulation of the drilling mud. The cost of holding the hole open for the several weeks necessary is usually unacceptable, and the only thermal data recorded in many cases are the bottom-hole temperatures one or two days after drilling has been completed.

Magnetic logging of bore-holes is quite practicable but has little application in oil search. Attempts have been made to use the magnetic polarizability of hydrogen nuclei (i.e. protons) as a measure of the hydrogen content of the wall rocks, but the results obtained are dominated by the effects of the drilling mud, and formation effects are small and difficult to isolate.

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4

Drilling for Oil

By J. W. JENNER

THERE are two basic methods of drilling for oil, the cable tool method and the rotary method. The former employs percussion and the latter a rotary, grinding action.

Rotary drilling is now the most common method, but sufficient cable tool rigs still exist in some parts of Eastern Europe and the USA to warrant a brief description of the method.

CABLE TOOL DRILLING

Cable tool drilling achieves penetration by pulverizing the rock. A drilling bit, rather like a big chisel, is attached to a heavy drill stem suspended by a cable from a cantilever arm, the walking beam, at the surface. The cantilever is rocked, imparting a reciprocating vertical motion to the drill stem and bit via the temper screw and the drilling line. By adjusting the length of the cable the bit is made to pulverize or chip the formation. The hole is kept partly filled with water to soften the formation and prevent caving. From time to time, as the hole is deepened and the bottom becomes full of cuttings, the bit is withdrawn and a bailer run in to remove the cuttings. The bailer is just a length of pipe with a disc or dart valve in the bottom, which opens on contact with solid material and allows it to enter. The bailer has to be run several times to remove all of the detritus present.

Steel pipe or casing is run into the hole once it reaches a certain depth or when hole conditions make it necessary. The casing is hung at the surface and lowered joint by joint as the hole is deepened. To do this the hole is deepened at least one joint length below the casing shoe and the bit is withdrawn. A special under-reaming bit, which opens out to a larger diameter than the inside of the casing, is then run and enlarges the hole, allowing the casing to be lowered.

Once the casing is in the hole a mud circulating system can be established. Mud is drawn from surface tanks and pumped via a flexible hose to a circulating head attached to the top of the casing. It passes down the casing and returns to the surface through the casing/borehole annulus, back to the tanks. A stuffing box, or gland, fitted to the circulating head allows the cable to move freely and prevents mud leakage.

A cable tool rig is shown in Fig. 1. It consists of a derrick to support the drilling line, the sand-line on which the bailer is run, and the casing line.

Wells have been drilled to 5000 ft using the cable tool method, but these days it is generally confined to much shallower operations.

THE ROTARY DRILLING SYSTEM

Until 1900 nearly all oilwell drilling was done by cable tool outfits. Since then the rotary system has been developed, and today very few cable tool rigs exist.

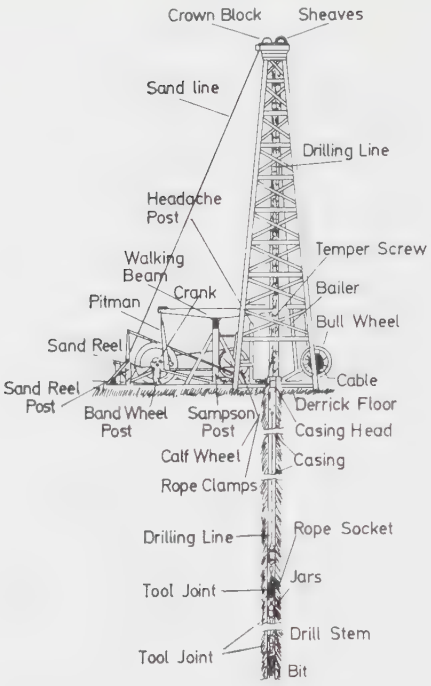


FIG. 1. Standard cable tool drilling system.

The rotary rig drills a hole by rotating a column of hollow steel pipes on the bottom of which is a bit which carves, chisels or grinds a hole, depending on the type of bit used. Drilling fluid or 'mud' is pumped through the pipe and out through the bit, returning to the surface via the pipe/borehole annulus, lifting the cuttings from the bottom of the hole, and carrying them to the surface. This will be enlarged upon later.

THE ROTARY DRILLING RIG

Rotary drilling rigs, whether designed to drill to 10 000 ft or 20 000 ft, for use on land or offshore, are basically the same and consist of:

(a) Power plant.
(b) The hoisting and rotating mechanisms.
(c) The drilling column or drill string.
(d) The fluid circulation system.
(e) Blowout preventers.
(f) Ancillary equipment.

A simplified diagram of a rotary drilling rig is shown in Fig. 2.

Power Plant

Until the mid-1930s nearly all drilling rigs were steam powered for simplicity, flexibility, and reliability. However, as depths increased, the size of the boilers

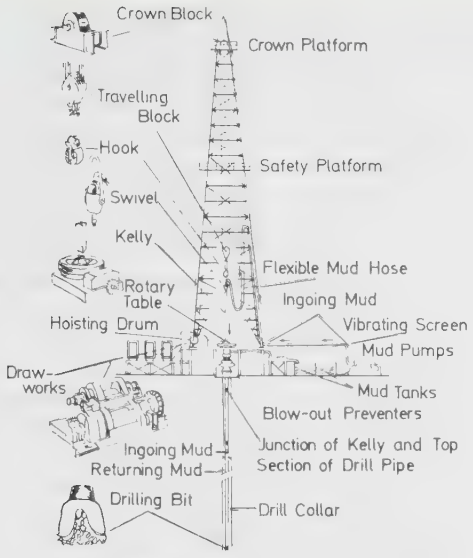


FIG. 2. Simplified diagram of rotary drilling rig.

and the amounts of fuel and water became uneconomic, and the internal combustion engine began to be used. This trend was aided in the late 1930s by the introduction of the fluid coupling and torque convertor which enabled the engines to run at their optimum speed and to supply the variations in power requirements.

Today, nearly all rigs are powered either by diesel (or multifuel) or by diesel/electric engines. Diesel or multifuel engines are normally used on small land rigs which have to be broken down and transported regularly from site to site. On remote exploration wells the fuel will be diesel fuel but on development drilling, gas from the field can be used. The size and number of engines on a rig will depend on the depth to which it is designed to drill; for example, a 5000-ft rig will need about 750 hp and a 15 000–20 000-ft rig will need up to 4000 hp. Offshore rigs and most modern heavy-duty land rigs are diesel-electric powered. The latest development in this type is the SCR (Silicon Controlled Rectifier) System. A.c. power is generated by the diesel prime movers and distributed, through the rectifiers, as d.c. power to the d.c. motors around the rig. Rigs with this system are more economic to run, since less generating capacity is required than the old d.c. rigs, where each d.c. motor was linked to a d.c. generator of similar capacity.

On large offshore platforms, such as those in the northern North Sea, the power for the rig is supplied from the main generating plant. In most cases gas turbines are the prime movers, utilizing produced gas from the reservoir.

Hoisting and Rotating Mechanisms

The hoist or drawworks is designed to raise or lower, at optimum speeds, the drill string and casing used on a well. On deep wells the casing load can be as

much as 350 tons. The hoist is essentially a high-speed, geared winch, the main component of which is a horizontal steel drum around which is wound the blockline. The drum is equipped with brake flanges at each end, generally water-cooled by internal circulation. The blockline is a multistrand wire rope, between 1 and $1\frac{1}{2}$ inch in diameter, which passes through a block and tackle arrangement inside the derrick of the drilling rig. The sheaves at the top of the derrick are fixed and are known as the crown block, and the others which move up and down inside the derrick vertically above the hole are the travelling block. Each block has up to five sheaves, and thus a 10:1 mechanical advantage can be obtained. The travelling block is moved by winding in or paying out the blockline on the drawworks. Attached to the travelling block is the hook, on which hangs the bail of the kelly swivel when drilling, or the elevators when hoisting or lowering pipe.

The drawworks is driven by chain, either from the engine compound, usually through a gearbox containing six gears, or by electric motors mounted behind it. Above and behind the main drum of the drawworks, is a second drum which holds the sandline, a smaller diameter ($\frac{1}{2}$ in) wire line which passes over a sheave near the top of the derrick and is used for running survey instruments, etc., into the well. Through the centre of the sandline drum, or core-reel as it is also known, is the catshaft, which rotates independently of the drum and has capstan heads or catheads on each end. The rotating cathead provides a source of power for picking up or moving small items of equipment inside or near the derrick when the other end of a rope attached to the load is wrapped around it.

All the various functions of the drawworks and ancillary equipment are controlled, via air clutches, by the driller at a console at the left-hand side of the drawworks.

The derrick is a fabricated steel tower, sufficiently strong to support the loads imposed by drilling operations. In the evolution of the rotary drilling method, the derrick that eventually evolved as being mobile, easy to erect or dismantle, and capable of efficiently removing and storing the drill pipe each time it was necessary to change the bit, was one that would handle 90-ft lengths (or stands) of drill pipe. Thus, with few exceptions, derricks are 130–145 ft high and are capable of supporting loads of up to 500 tons.

The drill string is rotated by means of the rotary table, which is located on the rig floor vertically above the well. Its two essential functions are to grip and rotate the drill string which passes through its centre, and to support the drill string when the travelling block is disconnected from it. It is, in effect, a strong steel annular ring with a spur gear on its lower surface. This engages with a pinion gear which is rotated by chain drive from the lay shaft of the drawworks. Some rigs have an independent rotary drive, either a small diesel engine or an electric motor on a diesel/electric rig.

The central hole in the rotary table, which varies from $17\frac{1}{2}$-in diameter, on a small rig to $47\frac{1}{2}$ in on a big offshore rig, is fitted with a hollow split, hinged, steel master bushing, which has an outside square at the top. This is to key the bushing to the rotary table. Smaller two-piece bushings, or bowls, having an inside taper, are keyed to the master bushing, forming a seat for the two-piece (separate) or three-piece (hinged) circular wedges called slips, which grip and support the drill string when it is released from the travelling block. Final connection to the drill string is provided by the kelly bushing, which fits around

the square or hexagonal cross-section kelly. The bottom of the kelly bushing is either square and fits into a square recess in the bushing in the rotary table, or has four cylindrical pins which fit into holes in the top of the master bushings, thus transmitting rotation from the rotary table to the kelly. In order to support the heavy loads imposed upon it, the rotary table is supported by heavy beams built into the rig substructure.

The Drilling Column or String

The drilling string consists of the kelly, the drill pipe, the drill collars and the bit.

The kelly is the topmost section of pipe and transmits the drive from the rotary table to the drill string. It is usually approximately 40 ft long, square or hexagonal in cross-section, has a right-hand thread connection at the bottom and a left-hand thread connection at the top. It is supported, via the swivel, by the travelling block, and slides downwards through rollers in the kelly bushing as drilling proceeds and the hole is deepened.

In the hole below the kelly is the drill pipe, made up of lengths of steel pipe (joints) screwed together by special leak-proof couplings. On the majority of rigs, the joints are between 30 and 32 ft long, allowing a 90 ft stand of three joints to be pulled from the hole and stood in the derrick. The top connection or tool joint on the pipe is female and is known as the 'box', and the bottom male connection is the 'pin'. At one time tool joints were screwed on to each end of the plain pipe but most modern pipe has flash welded pins and boxes. The tool joints have a larger outside diameter than the pipe to maintain the necessary strength. Several thread forms are used, but the most common is the sixty-degree taper of the API Internal Flush Joint (Fig. 3) which provides an unrestricted bore through the middle of the tool joint. The most common size of drill pipe is 5-in od for drilling down to $8\frac{1}{2}$-in diameter hole. Smaller hole requires smaller drill pipe, either $2\frac{7}{8}$ or $3\frac{1}{2}$ in od.

Between the drill pipe and the bit are the drill collars. These are heavy-wall cylinders of steel, approximately 30 ft long which concentrate weight immediately above the bit and maintain the drill pipe in tension. Drill pipe will buckle in compression causing hole damage, excessive wear and fatigue failures. The outside diameter of the drill collars varies from 12 in to, say, $4\frac{1}{2}$ in, depending on the diameter of the hole being drilled, and as many as thirty are run in order to get sufficient weight on the bit. They have similar box/pin connections to those on the drill pipe, machined into each end.

Both drill pipe and drill collar connections are precision-made to rigid tolerances, providing a robust, pressure-tight seal at the connections and rotational stability and strength when in the hole. Great care is exercised when handling them, to prevent thread damage, which would destroy the pressure seal and cause rotational failure in the pipe.

Many thread forms have been developed and used since the beginning of rotary drilling and attempts have been made by the American Petroleum Institute to standardize on a few. These are known as API threads, e.g. API Internal Flush, API Regular. These threads are always cut to the same specifications, and a pin and box of the same size, made in different parts of the world, will always match.

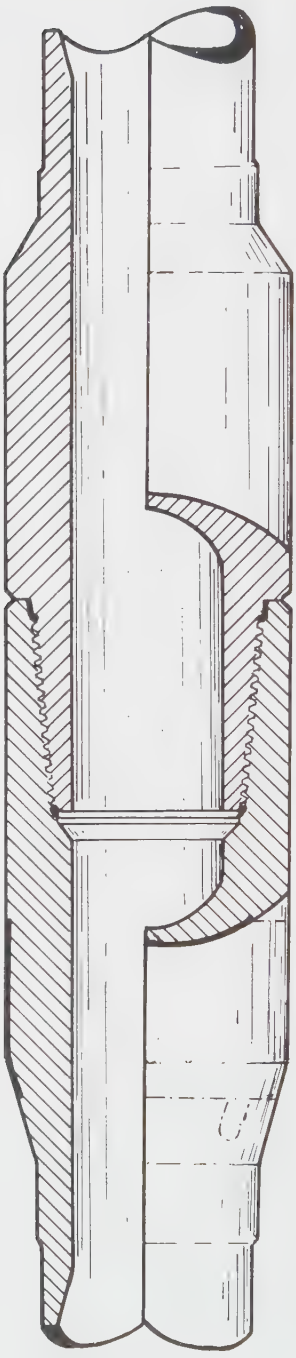


FIG. 3. API internal flush tool joint (tapered shoulder).

At the bottom of the drilling string is the bit. This has taken several forms in the past, but the majority of bits today are of the tri-cone type (Fig. 4(a)). Some drag or fish-tail bits are used in very soft formations such as are found in the Gulf Coast, Louisiana. The tri-cone bit utilizes three forged steel conical cutters whose axis of rotation is slightly offset from the centre of the hole. As the bit is rotated the cutters rotate and the cutter teeth dig and gouge out the formation. Long-tooth bits are used for soft formations and bits with shorter teeth for hard formations. In hard rock the teeth of the bit are effectively chiselling at the bottom of the hole as heavy weight is required to drill. For very hard rock drilling, bits with chisel-shaped tungsten carbide inserts have been used. These crush the formation as the bit rotates. There are two types of tri-cone bit, the conventional and the jet. The former has fluid passages through the centre, directed on to the cutters, for washing off drilled formation, and the latter has jet pockets into which variable size jets can be fitted. These jets direct the fluid circulation on to the bottom of the hole where it jets away the cuttings. In soft formation the jets erode the bottom of the hole, increasing the penetration rate and prolonging bit life. The jet sizes are variable so that the pressure drop at the bit can be maintained at the optimum for a given circulation rate, thereby concentrating the maximum possible hydraulic horsepower on the bottom of the hole.

Diamond bits are also used to drill medium to hard formations. Industrial grade diamonds are set into a matrix, in such a way that when the bit is rotated, the complete area of the bottom of the hole is exposed to the cutting action of at least one diamond. This cutting action can best be described as scraping away a small piece of formation. The amount removed per revolution is dependent on the size of the diamond, its exposure from the matrix, and the hardness of the formation. Optimum fluid circulation is also necessary to clean and cool the face of the bit. Insufficient fluid will result in 'burning' of the bit; too much will lift the bit hydraulically off the bottom of the hole (Fig. 4(b)).

Diamond bits are designed to drill formations of a particular hardness. The stone sizes used vary from three-carat stones to two carat stones. They are most economically used with turbodrills (see later under Turbodrills). Diamond bits are very expensive, costing twenty to thirty times the price of a tri-cone bit but as they drill as much formation as maybe four or five tri-cones, the economy is in the saving of the rig time required to change bits. This is particularly applicable in the case of the very expensive platform rigs or semi-submersible rigs as operate in the North Sea. Some saving is also made from the value of the re-usable diamonds salvaged from the used bit.

A recent development in bit technology is the use of 'Stratapax', small plates of tungsten carbide coated on one side with a layer of diamond particles or dust. These are brazed into a similar matrix as is used for diamond bits, sometimes in combination with diamonds. These bits have been particularly successful in combination with turbodrills in both North Sea and Arabian Gulf drilling.

The Fluid Circulating System

The heart of the fluid circulating system is the mud pumps. On deep land rigs and on most offshore rigs there will be two 1300 or 1600 hp pumps. They are normally duplex double-acting, reciprocating, or the more modern triplex,

Hughes Tool Co. Ltd.

FIG. 4(a). Drilling bits.

plunger, single-acting pumps. On a diesel land rig one pump will be driven by multiple-V-belt or chain from the main drawworks engine compound and another will have its own independent motors. On smaller land rigs with lower power pumps, both can be driven from the compound. On modern heavy diesel/electric rigs each pump has two electric motors with combined output of 1500–1600 hp.

The duplex pump is fitted with removable liners. By changing the liner and piston size a variable pressure/volume output can be obtained at a fixed power input. Modern pumps can give up to 600 gal/min at 4500 psi, thus facilitating jet drilling in large diameter holes, and turbodrilling in the smaller diameter hole. The valves and valve seats are designed to cope with abrasive drilling fluids and are made easily replaceable in case of damage.

The mud pump draws mud from the surface circulating or storage tanks and pumps it to the stand-pipe, a 4 to 6-in diameter steel pipe about 50 ft long, fitted vertically to the side of the derrick. From there is passes via the flexible kelly

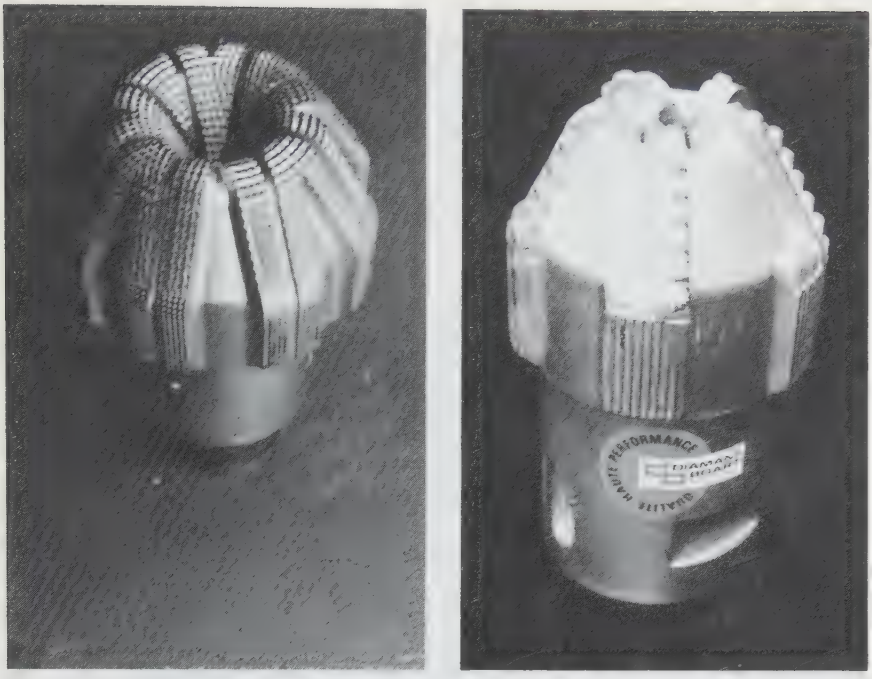


FIG. 4(b). Typical diamond bit (left), Stratapax bit (right). Courtesy of Diamant Boart S.A.).

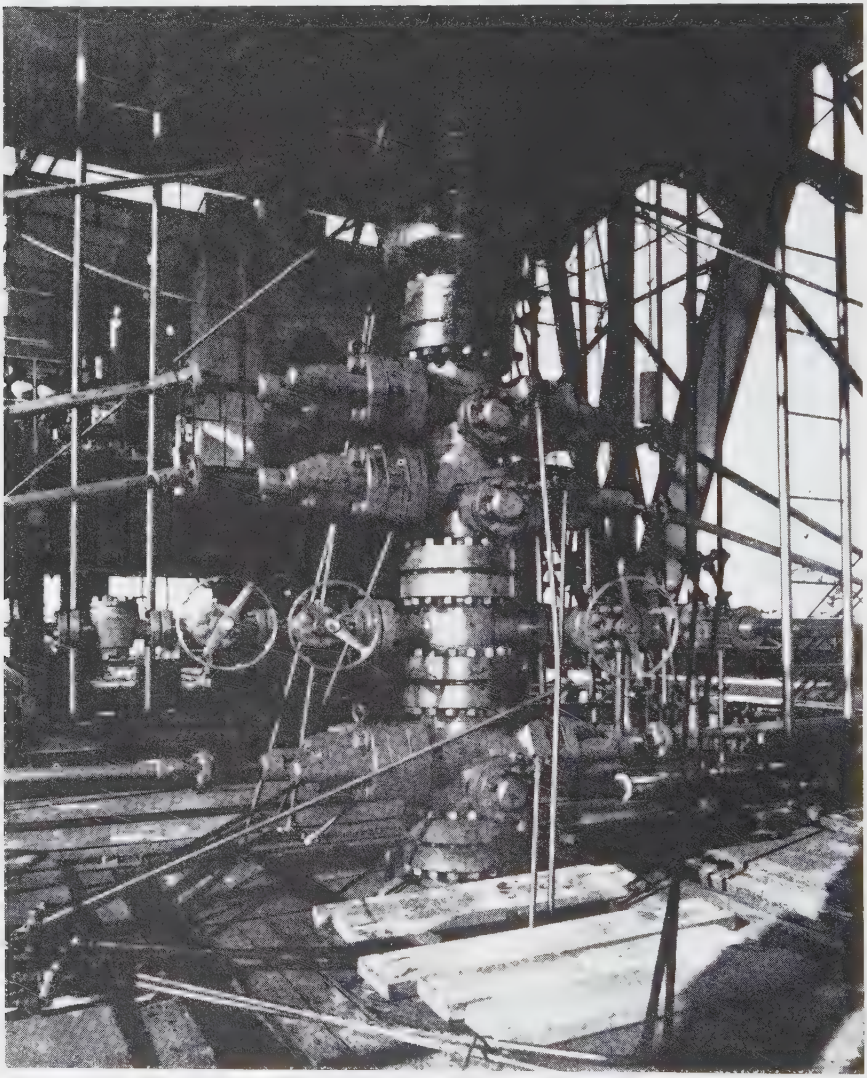
hose to the swivel. The kelly hose can be made up of steel pipe with swivel joints, but is more usually 4-in armoured rubber hose between 50 ft and 60 ft long. This allows the kelly and swivel to be picked up nearly to the top of the derrick without damaging the hose. The swivel hangs by its bail, an inverted steel U, from the hook beneath the travelling block, supporting the load of the drill string, allowing it to rotate and providing a sealed conduit for the drilling fluid from the kelly hose to the kelly. The load is taken on a tapered roller thrust-bearing and a rotating fluid seal contains the fluid. The bottom connection on the swivel is a left-hand threaded pin which screws into the top connection of the kelly. The thread is such that it will not unscrew when the kelly is rotated to the right.

From the swivel, the fluid passes down the kelly, drill pipe and drill collars, and through the jets in the bit on to the bottom of the hole. From there it lifts the cuttings through the annulus to the surface, where it is conducted from the hole through a vibrating screen or shale shaker back to the storage tanks. The shale shaker is a fine wire-mesh screen through which the mud is passed to remove cuttings.

Other items included in the fluid circulating system are the de-sanders and de-silters. These are vortex cones which centrifugally remove undesirable materials that are fine enough to pass through the screen on the shale shaker. Equipment for de-gassing the mud in circulation is also standard equipment on modern drilling rigs.

Blowout Preventers

During drilling blowout preventers (Fig. 5(a)) are connected to the top of the wellhead. These are used to shut in and control the well in the event of gas or oil being encountered at pressures higher than those exerted by the column of mud in the hole. They consist of two or three ram preventers and one bag-type preventer for onshore or jack-up rigs and up to five ram preventers and two bag-type preventers on sub-sea systems used on drill-ships or semi-submersible rigs. Their working pressure is 3000, 5000, 10 000 or 15 000 lb/sq in, depending on the well depth and pressures expected.



Cameron Iron Works Ltd.

FIG. 5(a). Typical blowout preventer stack on land well.

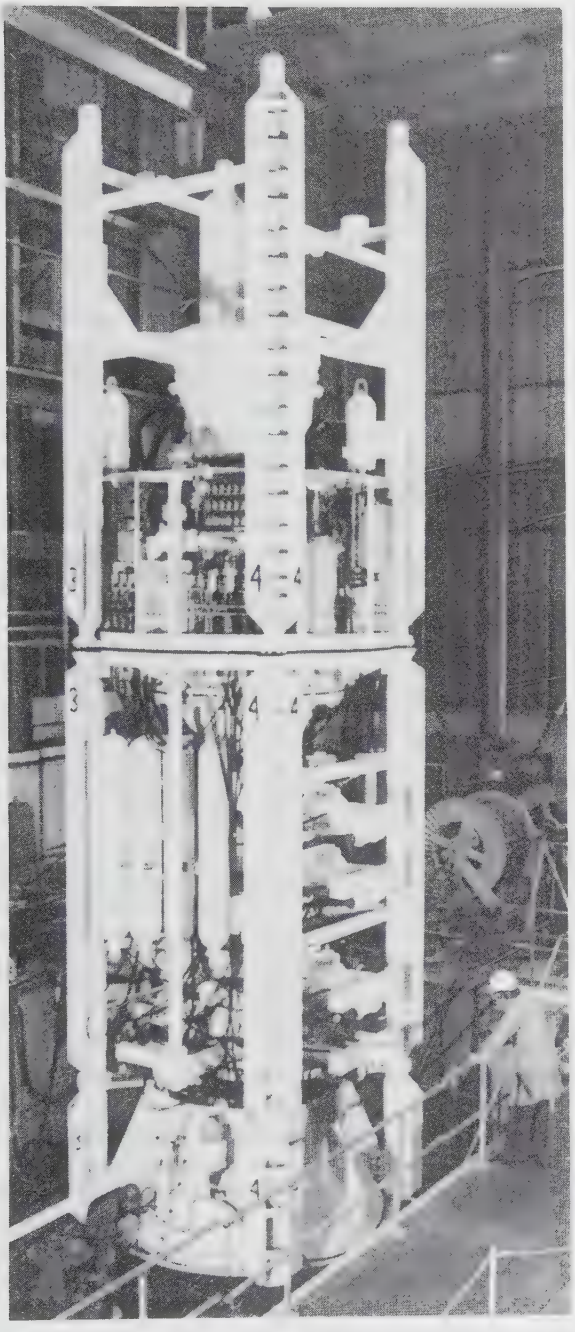


Fig. 5(b). Sub-sea blowout preventer stack.

The ram-type preventer is basically a double hydraulically-operated valve with one ram (or gate) on each side of the borehole.

The rams have either a straight leading face to shut off on each other (known as blind rams) or a recessed face to fit around the body of the pipe in use, be it drill pipe or casing. The leading face and top edge have rubber seals to shut off against the pipe and the body of the preventer.

In the open position the rams are withdrawn into the body of the preventer clear of the borehole. In the closed position they are moved across the borehole to close off on each other or on the pipe through the middle of the preventer.

The topmost preventer is usually of the bag type that will close around any shape. It consists of a thick annular rubber ring sitting in the bowl of a conical-faced piston. In the open position the bore through the middle of the preventer is clear. When closed, the piston moves upwards, squeezing the rubber against the body of the preventer, causing it to flow into the bore and moulding it into a seal around whatever shape it encounters, e.g. the kelly, 10-in drill collars or 5-in drill pipe. By adjusting the closing pressure on the piston it is possible to move the pipe through the rubber which adjusts its shape as required.

The blowout preventers are hydraulically operated from a control panel located on the rig floor. A second remote control panel is situated some way from the rig for use in emergencies when the rig is unapproachable.

The blowout preventer stacks, as they are known, used on land rigs or offshore platform or jack-up rigs (Fig. 5(a)) are essentially the same simple one-bag type and three-ram type systems, weighing between 20 and 25 tons when assembled. The stacks used on floating rigs (Fig. 5(b)) are more complex assemblies, as they are built into a guide frame which contains hydraulic control equipment, an emergency control system and other instruments. They are normally of 10 000 psi and sometimes 15 000 psi working pressure, and comprise at least four sets of rams and two bag-type units. The all-up weight of a sub-sea blowout preventer stack, which has to be lowered to the sea-bed, can be as much as 150 tons.

Connected into the side of the ram-type preventers, usually below the blind rams, are the kill and choke lines which are used to control the well in the event of any imbalance between the drilling fluid column pressure and the formation pressure. Both lines are high-pressure 2 or 3-in pipe, the kill line being connected to the mud circulating system and the high pressure cement pumps, and the choke line leading to a back-pressure control manifold and mud de-gasser unit.

In the event of high pressure kick with the drill string in the hole the blowout preventer is closed around the drill pipe and the mud is circulated down the drill string and back to the mud tanks through the choke line and back-pressure manifold. The manifold consists of a series of valves and chokes. A choke is a type of valve with a conical gate and matching seat concentric with the bore of the valve. The choke can be adjusted to give whatever orifice is required to provide a back pressure on the well in order to control it, while circulating and raising the specific gravity of the drilling mud by addition of heavy material, to hold back the kick. There are usually at least two chokes on a back-pressure manifold, either of which can be isolated to permit the cone and seat to be changed.

If a kick or blowout occurs with the drill string out of the hole, the blind rams

are closed and heavy mud is pumped to the well through the kill line. Any gas can be bled off through the choke line, and fluids are usually squeezed back to the formation.

The correct installation of the wellhead and the operational reliability of the blowout preventers are essential for the safety of any well. The wellhead is thoroughly checked and pressure-tested when installed, and the preventers are functionally tested and pressure-tested at frequent intervals throughout the drilling of a well.

Ancillary Equipment

A.c. power plant for rig lighting and domestic power on remote locations, air compressors, water pumps, bug fans for tropical locations, heaters for cold climates are all necessary items of ancillary equipment, which are normally available on any offshore drilling unit.

DRILLING PRACTICE AND PROCEDURES

Personnel

The crew of a rotary drilling rig normally consists of:

1. The driller, who operates the drawworks, rig machinery and pumps, and is in charge of, and responsible for, his shift.
2. The derrickman, the most senior rigman, who works in the derrick about 90 ft above the rig floor, latching or unlatching the drill-pipe elevators when pipe is pulled from the hole or run back into it.
3. Three or four floormen, who set the slips to hold the drill pipe, handle the tongs or wrenches for screwing up or unscrewing the drill pipe, latch and unlatch the elevators, etc., and generally handle equipment around the rig floor. The number of floormen will vary from rig to rig, depending on size and location (on land or offshore).
4. The motorman who maintains the mechanical equipment around the rig.
5. The electrician who maintains the electrical equipment around the rig.

Three 8-hr shifts or tours (pronounced towers) per day are normally worked on a land rig close to civilization. On more remote locations with living quarters and on offshore rigs, 12-hr tours are worked, with provision for regular time off.

The operation of a land rig is controlled by a foreman called a toolpusher. Offshore a senior toolpusher is in charge of the rig and there are normally 'tourpushers' working 12-hr shifts, controlling the drilling crew.

There are also general labourers, known as roustabouts, employed around the rig, particularly offshore, whose jobs are to unload chemicals, casing, cement, and general supplies from the trucks or supply boats and generally to maintain the rig area.

The increased complexity of the equipment used, particularly on floating rigs, has led to the inclusion of technical specialists in the drilling crew. These include sub-sea wellhead engineers, to maintain blowout preventers, etc., and

barge engineers responsible for the marine operations, i.e. stability, trim, etc., of the floating rigs.

The majority of drilling rigs are owned by Drilling Contractors who drill on behalf of the company or companies (known as the Operator) who hold the licence to drill the well. Normally the Operator has a drilling supervisor on the rig who is responsible for drilling the well and ensuring that the Operator's programme and instructions are carried out.

Drilling

On land

Before erecting and rigging up the drilling rig, a hole is dug at the location about 10 ft square and 6 ft deep, and lined with concrete or timber. This is called the cellar whose function is to accommodate some of the wellhead equipment and preventers below ground level, to reduce the height of the rig floor above the ground. With the rig in place the rathole and mousehole are drilled if necessary. The rathole is a length of pipe into which the kelly and swivel are placed when not attached to the drill string. It is set somewhere on the standpipe side of the rotary table and inclined towards it, so that the hook can easily pick up the bail when required, yet the swivel is clear of the centre line of the hole. The mousehole is a similar length of pipe set vertically on the forward side of the rotary table into which is placed the next joint of drill pipe to be added to the drill string. The bottom end of both pipes has to be set into a hole drilled by a small portable drilling machine.

Drilling is started by attaching a short drill collar and a large bit to the kelly and drilling a hole to about 50 ft. A length of large-size casing is run into this and cemented to the formation. This is called the conductor. It reaches to just below the rotary table and has a side outlet near the top, connected to a smaller pipe, which carries the mud away to the vibrating screen. Drilling then proceeds, using the largest possible bit until a compact formation is reached in which to set the surface casing, which is designed as an anchor for the blowout preventers. Casing is run into the hole and cemented to the formation by pumping the volume of neat cement required (i.e. volume of annulus between casing and hole) into the casing, then displacing it out of the bottom and into the annulus by filling the casing with mud. There is a special non-return valve in the bottom or shoe of the casing to prevent the usually higher density cement from running back and displacing the mud out of the casing, once pumping has stopped. Casing is thin-walled steel pipe in 30 to 40-ft sections, with threaded connections, which, when cemented into the hole, holds back the formation and any fluids or gases, and forms a pressure-tight container.

With the blowout preventers set, the hole is then deepened to an impervious formation above the production zone where the intermediate casing is run and cemented, to shut off any permeable formations and to prevent any unconsolidated formations from caving into the hole. After that the well is drilled through the production zone and the production casing (or oil string) is run and cemented into position.

The casing sizes used depend upon the final depth of the well, whether it is an exploration or production well, and how much oil or gas the well is likely to

produce. A deep exploration well or a big production well (5000 tons/day would have 30-in od conductor, $18\frac{5}{8}$ or 20-in od surface casing, $13\frac{3}{8}$-in od intermediate casing and $9\frac{5}{8}$-in od production casing. Shallow wells, or smaller producers could have a maximum of 20-in conductor, $13\frac{3}{8}$-in od surface casing, $9\frac{5}{8}$-in od intermediate casing and 7-in od production casing, to as little as $10\frac{3}{4}$-in od surface casing and a 5-in od production string.

As drilling proceeds and the well is deepened a new joint of drill-pipe has to be added to the drilling string for every 30 ft of hole drilled. To do this the rotary table and the mud pumps are stopped, and the drill string is picked up by the drawworks until about 3 ft of the top joint of drill pipe is above the rotary table. The slips are then dropped into the table around the pipe and the drill string is hung on them. Two large spanners, or tongs, are then latched on to the string, one on the kelly and one on the drill pipe, so as to unscrew the connection. Each tong is suspended over a sheave near the top of the derrick, by wire line, on the other end of which is a counter-balance weight. This permits easy movement of the tongs. The arm of each tong is approximately 4 ft long. A wire rope connects the end of each tong arm to a power take-up built into each cathead on the drawworks. To break the connection between the kelly and the drill pipe, the driller operates the clutch on the cathead and pulls in the line on the tong on the kelly, until the connection starts to unscrew. The other tong has a fixed-length back-up line to stop it turning with the pipe. Once the connection starts unscrewing the tong on the drill pipe is released and the driller slowly rotates the rotary table and the drill string, unscrewing the drill pipe from the kelly, which is held by the other tong. Once clear, the kelly is picked up a short distance and the bottom is swung over and stabbed into the joint waiting in the mousehole. Around this joint of pipe are four or five wraps of spinning chain, one end being held by a floorman, the other end running to a cathead power take-up. The chain is reeled in, rotating the pipe and screwing it on to the bottom of the kelly. The connection is then tightened by the tongs, and the kelly, with the new joint, is picked up by the drawworks and stabbed into the drill pipe at the rotary table, where it is screwed up and tightened in the same way. This whole operation is called 'making a connection'.

As the kelly is 40 ft long and the joints of drill pipe are 8 to 10 ft shorter, there is sufficient room in the hole, when making a connection, to lower the new joint and get the kelly bushings into the rotary table. It may be necessary under some conditions to circulate cuttings away from the bottom as the string is lowered.

When the bit wears out and has to be replaced, the crew have to 'round trip' the pipe, i.e. pull out, change the bit, and then run in. The kelly is disconnected as above, lowered into the rathole and the hook unlatched from the swivel bail. The travelling block is then lowered until the elevators, which hang on links below it, can be latched around the drill pipe below the upset of the tool joint. The drawworks then hauls the blocks up the derrick until a stand of three joints of drill pipe is above the rotary table. The string is landed in the table, the stand unscrewed and picked up slightly by the elevators. The floormen then swing the bottom end of the stand away from the table and it is lowered on to the rig floor, at which time the derrickman, up the derrick, unlatches the elevators, pulls the top of the stand over and racks it against the side of the derrick. The elevators then descend to the rig floor level and pull the string back another 90 ft, and so on until all the drill pipe and drill collars are out of the hole, and the bit can

be changed. The process is then repeated in reverse to get the bit back to the bottom of the hole and restart drilling.

Trip time is unproductive time with regard to drilling, so good teamwork between members of the crew is essential to keep it to a minimum. Pulling the pipe quickly from the hole, or running it in too quickly can be dangerous. The former swabs the hole, reducing the pressure on the formation, allowing gas and oil to come in and cut the mud. Running the pipe in too fast exerts a plunger effect on the bottom of the hole which can pressurize it and break it down, leading to mud losses and collapse of the hole.

The process of drilling requires skill and experience, although much of the art has now been replaced by science. Even the worst-equipped rigs have a weight indicator, which shows the driller how much weight he has on the bit, and a pump pressure gauge. A well-equipped modern rig will also have pump stroke indicators, rotary speed and torque indicator, and a mud pit fluid-level indicator which help the driller. It will also have a tong torque gauge showing how much torque he is applying when screwing the drill collars together. Drill collar connections all have recommended make-up torques to ensure correct tightening.

Despite careful drilling and regular inspection of drill strings, fatigue failures of drill pipe or collars do occur from time to time; also bits can fail, leaving cones and bearings in the hole. Another source of trouble is the hole itself, causing sticking of the pipe either by crooked hole, collapse of formation or by differential sticking (the pipe being held against the side of the hole by the difference in pressure between a porous formation and the mud column).

When these mishaps occur fishing is necessary in order to recover the pipe or junk left in the hole. In the case of stuck pipe the free section has to be released first. There are many methods and tools employed for fishing, too numerous to detail here. The method used depends on the nature of the fish and which tools are available. Obviously, it is not desirable to fish for very long because of the expense, and very often it is cheaper to cover the fish with cement and sidetrack or redrill the hole past it.

Part of the art of drilling is the avoidance of trouble and the early recognition of the development of dangerous conditions.

Offshore

The basic operation of drilling a hole on an offshore location is exactly the same as on a land well. The only difference is in the method of connecting the well to the rig which is either floating or standing above the location.

There are four basic forms of offshore rig:

(a) Fixed multi-well platform
(b) Mobile jack-up platform
(c) Drill ship
(d) Semi-submersible platform.

(*a*) *Fixed multi-well platform*. This is the simplest offshore rig and is normally installed on a known field to drill development or production wells. The platform (Fig. 6) consists of a welded tubular steel structure, pile-driven into the sea-bed, supporting what is basically a land drilling rig, and production

Fig. 6. Fixed multi-well platform.

equipment, power plant and accommodation at a safe height above sea level. This height will depend on the geographical location, but is normally at least 50 ft above mean sea level. The size of the platform varies considerably, depending on water depth and the number of wells to be drilled, but a deck area of 150 ft × 150 ft is a good average. In addition to the rig, the platform will also support living quarters for the crew, say fifty men, cranes and storage racks for drill pipe, drill collars, casing and probably production equipment. The whole thing is built in sections at a nearby port, transported to the location by barge

or floated out and erected by an offshore work barge with a crane that will lift loads of up to 2000 tons.

The number of wells drilled from this type of platform varies from place to place. Fixed platforms are found in the Gulf of Mexico, North Sea, Bass Strait, Adriatic, Persian Gulf and US Pacific Coast, and support from 10 to 40 wells. The wells are drilled directionally, possibly drilling into the pay zone up to 8000 ft horizontally away from the platform. On the platform the wellheads can be as close together as 6 ft, and the rig itself is mounted on skids so that it can be moved from position to position as wells are completed. Some platforms hold two rigs working simultaneously.

There is very little difference between a land well and a well from a platform. To start the well, a welded conductor pipe, anything from 20 to 30-in diameter is driven about 100 ft in to the sea-bed and cut off just below the rotary table. This connects the sea-bed with the rig. Drilling then proceeds as on land, the wellhead being set on a cellar deck approximately 15 ft below the main deck.

Once all the wells are drilled and completed the crane barge returns to the platform and lifts off the drilling rig and associated equipment, leaving only production equipment on board. The rig can then be moved to another platform.

(*b*) *Mobile jack-up platform*. This is the most economic mobile offshore drilling unit. It consists basically of a dumb barge which can raise itself out of the water on legs to well above storm wave height, and upon which is mounted a drilling rig. Most jack-up units have either triangular or matchbox-shaped hulls with either three or four lattice or cylindrical column legs. Jacking is by either a low-geared electrical rack and pinion system or hydraulic, attached to the chords of the lattice legs or racks on the cylindrical legs. Jack-up rigs vary in water depth capacity from special shallow draft units for sheltered, inshore waters to the very large, deep-water, exposed environment structures. The latter are designed to operate in 300 ft of water, in wind speeds of 100 miles/hour and 70 to 80-ft waves. Hull sizes vary between 250 ft × 200 ft × 26 ft deep and 200 ft × 170 ft × 16 ft deep.

There are two types of jack-up rig. The older style had the derrick and drawworks located on a substructure which could be moved over a slot, approximately 40 ft wide by 30 ft deep, in the stern of the barge. The newer style which is increasingly popular has the derrick and drawworks located on cantilever beams 25 to 30 ft high which can be jacked out over the stern of the barge (Fig. 7). This is a more versatile arrangement. The main upper deck is the pipe rack and storage area, and the mud pumps, tanks, generators and other machinery are located within the hull. The accommodation is located on the forward end of the barge, and is generally all on or above main deck level. A helicopter landing deck is located on top of the accommodation. Jack-up barges have to be moved by tugs although some self-propelled units have been built.

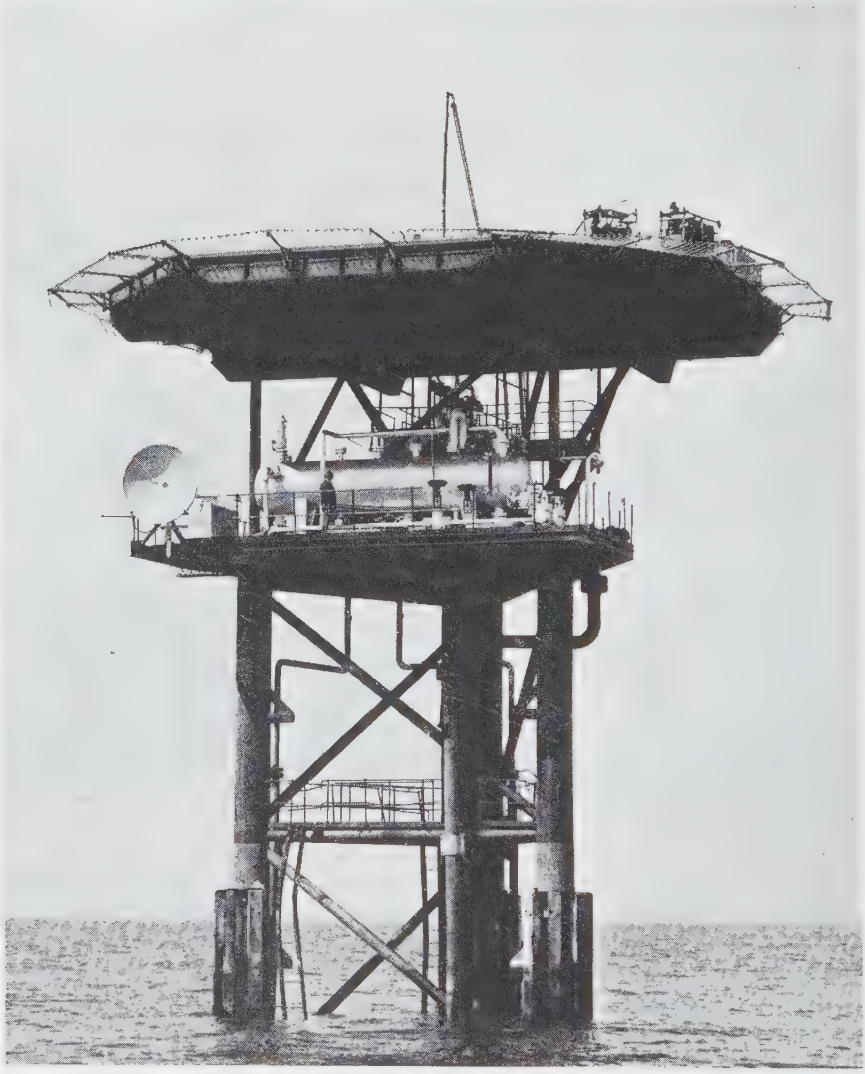
The jack-up barge is towed to location, the legs are dropped or jacked down to the sea-bed, and then the hull is raised out of the water some 50 to 60 ft. Before drilling starts, the legs have to be driven into the sea-bed by pre-loading each one in turn by moving ballast water in the hull, to ensure that settling does not occur during drilling. The well is started either by driving a 30 to 36-in diameter conductor pipe to approximately 100 ft below the sea-bed or drilling

Fig. 7. Jack-up platform.

a large (36-inch) hole and running and cementing the conductor in place. Drilling then proceeds as on a platform with the blowout preventers and wellhead inside the slot or below the cantilever. If the well is an exploration well, the rig will probably use a special system which allows the casing to be hung just above the sea-bed. All the casing strings are continued right back to the barge but in the event of the well being a discovery, it can be temporarily plugged, the casing unscrewed and removed from the hangers above the sea bed, and a protective cap installed. The barge then jacks down and moves

away, and a multi-well platform can be built over the well, which is re-completed back to surface. The jack-up barge is also used to drill individual development wells. In this case, on completion of the well, the rig and derrick are jacked forward, clear of the slot, and the barge is jacked down, leaving the well sticking up out of the sea. A protective tower or jacket, providing access to the wellhead, is then erected around the well (Fig. 8).

In less than 250 ft of water the jack-up rig is the most economic offshore drilling outfit. Once on location the well can be spudded in (started) within hours of arrival, and drilling can proceed unhindered except by the most



BP Photo

FIG. 8. Single well tower, Arabian Gulf.

extreme weather. Once the well is completed the barge can be jacked down, moved to a new location, and be drilling again within hours of positioning. Only bad sea conditions during moving will delay operations.

(*c*) *Drill ship.* There are several types of drill ship. Some are specially-built vessels, others are converted tankers or similar vessels; some are self-propelled, some are not, some require anchors to maintain location, others are dynamically positioned. However, they are basically the same, having a ship or barge hull with a drilling rig positioned over a hole in the middle. The hole is known as the moon-pool and is between 20 ft and 25 ft in diameter. The derrick is specially designed to withstand the movement imparted by the ship's motion in rough weather and the travelling blocks are guided by a track. Some drill ships have a mechanical handling device for drill pipe, which lays the pipe down in stands on the deck during a trip, instead of standing it in the derrick.

On arrival at the location the drill ship is moored by up to eight anchors, with the bow heading into the direction of the prevailing wind. Drill ships which are dynamically positioned are equipped with bow and stern thrusters which can move the vessel sideways. These and the main engines are controlled by a computer which maintains location relative to signals from radio beacons ashore, or from radio or sonic beacons on the sea-bed near the well location.

In order to drill the well from a rig that is moving with the tide and the waves, the wellhead and blowout preventers are set on the sea-bed, and the well is connected to the vessel by a relatively flexible steel riser pipe. A heavy steel guide structure is first of all run to the sea-bed on the drill string. The guide structure has two or four guide wires that lead back to just below the rig floor, where constant-tension hydraulic tensioners keep them taut, allowing for the rise and fall of the vessel. The hole for the conductor or surface string is then drilled and the casing with the first part of the wellhead run down the guide wires, into the hole and cemented into position. The blowout preventer is then run and latched into the guide structure with its attendant control hoses. It is hydraulically operated from the rig and has a dual system in case of damage or failure. The riser or marine conductor is then run and latched on to the top of the blowout preventer, establishing the connection from the well to the rig. The riser is held by wire ropes from four riser tensioners. These are pneumatic pistons which maintain a constant tension in the ropes as the vessel rises and falls with the tide or seas. The topmost joint is telescopic, one end being fixed to the rig and the other to the riser, allowing the length to vary as required.

Drilling then proceeds as normal, except that the wellhead is on the sea-bed. Anchored drill ships can operate in water depths of up to 1500 ft, restricted only by the length of anchor cable required and their ability to store and run sufficient riser pipe, usually in 16-in od by 40-ft long joints.

The more advanced dynamically positioned drill ships have been used to drill in excess of 4000 ft of water. They do not require any moorings, and only riser capacity restricts their potential water-depth capability. As they are dynamically positioned the guide lines for running and pulling the sub-sea equipment are not required. A combination of TV equipment, underwater orienting and jetting tools, and the ship's ability to manoeuvre are used to establish the wellhead and run and retrieve the blowout preventers and riser.

The drill ship, if self-propelled, is highly mobile and is particularly suitable for drilling one or two exploration wells in an area and then moving quickly to

another location many miles away. By doing this they can also take advantage of only operating in the good weather periods, where possible.

(*d*) *Semi-submersible platform* (*Fig. 9*). This type of barge is a free-floating structure, having a large mass but small water-plane area, resulting in a natural period of motion longer than the largest wave periods. It generally consists of a single deck housing a drilling rig, power house, accommodation, etc., supported by large diameter (20 -35 ft) vertical cylindrical columns connected to either horizontal cylindrical or larger diameter footings. The footings and columns can be ballasted or de-ballasted to alter the draught or the trim as required. Semi-submersible barges are normally very large, the latest units being used in the North Sea are 230 ft × 200 ft at maindeck level, with 30-ft diameter caissons, and measure 130 ft from main deck to the bottom of the footings. The top of the derrick is 200 ft above the main deck.

The barge is towed in the de-ballasted position to the location, where it is moored by eight or nine very large anchors and ballasted until it sinks to the drilling position. In this position the footings are well below sea level and the barge is virtually unaffected by wave action. Only high winds and long swells cause any serious movement.

Fig. 9. Semi-submersible platform.

The drilling method is the same as that of the drill ship, with the blowout preventers and wellhead on the sea-bed, the only difference being the increased length of the riser, from sea level to below the rig floor.

The semi-submersible rig can operate normally in up to 1500 ft of water. Again this is dependent on the capacity of the mooring system and the unit's ability to handle and store riser joints.

Most modern units are self-propelled and do not need tugs for short moves or manoeuvring near a location. Dynamically positioned semi-submersible units are in existence. The water-depth capacity of these units is increased as moorings are not required.

Both types of floating unit are expensive to build, the latest price for a semi-submersible being around £50 million.

Drill-stem Testing

A drill-stem test is the temporary completion of a well during drilling, or after setting casing, to measure formation pressures and to obtain samples of formation fluids or gases for evaluation.

The test is carried out in open hole or through casing perforations. The testing string usually consists of: a tailpipe of drill collars, some perforated, containing down-hole pressure recorders; a packer for either open hole or casing, which when set isolates the annulus above the packer from the hole or perforations below it; a testing valve which controls the flow; a down-hole control valve, operated by rotation or reciprocation of the drill string; a safety joint, jars, and a circulating valve. Drill pipe is run to surface and a flow control valve assembly is fitted just above the rotary table.

The test string is run into the hole either empty or containing a calculated head of water. The latter allows a sufficient differential pressure for the well to flow, but provides a cushion against a sudden surge when the testing valve is opened. This could break down the formation under test, cause the packer rubber to extrude and fail, or cause the formation behind the packer rubber to fail. The test string is run into the hole and the packer is set, either by standing the tailpipe on the bottom of the open hole, or by hanging the packer on the inside of the casing. The testing valve is then opened, normally by setting weight on it, and well fluid is permitted to flow through the perforated tailpipe and into the test string, to obtain an initial flowing pressure. After a few minutes the down-hole control valve is closed, by either reciprocating or rotating the drill string, and an initial closed-in pressure is obtained. After a short period the valve is re-opened, allowing the well to flow. A final flowing pressure is recorded at this time and fluid or gas samples are collected. The control valve is then closed and a final closed-in pressure is recorded. The final operation of the down-hole control valve connects the annulus with the inside of the test string, allowing the fluid inside the drill pipe to be circulated out and replaced with mud. The string is then picked up, the packer is released and pulled out, recovering the pressure-recording instruments. A sample of reservoir fluid or gas is trapped in the drill collars between the testing valve and the control valve. Jars are included in the string to bump the packer free if necessary. If the control valve should become plugged by pieces of formation

during the final circulation, the circulating valve higher in the string is operated and circulation is continued.

The above method applies principally to land wells or to offshore wells drilled from jack-up or platform rigs. If a similar test is required on a well drilled from a floating rig, a more sophisticated system is used. As an emergency might occur, usually the onset of bad weather, during a test, it is necessary to be able to disconnect the riser from the sea-bed blowout preventers and move the rig away without leaving the well open. To permit this, similar testing tools to those described above are utilized in conjunction with a sub-sea testing wellhead, which is landed inside the blowout preventers and is hydraulically controlled from the surface. As the testing valves can no longer be operated by reciprocation or rotation of the test string, they are operated by applying pressure to the annulus between the last casing string and the testing string. This annulus is sealed at the bottom by the packer and at the top by closing the blowout preventer rams around the testing wellhead. This obviously restricts testing from floating rigs to cased hole tests.

Directional Drilling

It is not always possible, because of topographical and legal problems, to drill vertically into an oil or gas reservoir. The required bottom of the hole may be under a lake or river, just off the coast, under a roadway or town or under an area where legal access to the ideal location is barred. In order to drill wells under these conditions, directional drilling is needed. Using this technique it is possible to direct the hole into a relatively small target up to 8000 ft away horizontally at 10 000 ft depth. This method is also used to develop a field from an offshore multi-well platform, and on the Alaskan North Slope tundra where surface and climatic conditions make it desirable to drill several wells from one location.

The basic well programme, casing size, etc., are the same as those for a vertical well, but with special equipment and techniques the angle of the hole from vertical is gradually increased in a pre-determined direction. The first 1000 ft or so are usually drilled vertically to permit the running of the large surface casing, and the well is then kicked off in the required direction. Until fairly recently a whipstock was used to deviate wells. This consisted of a tapered steel wedge which was run to the bottom of the hole and orientated so that it pushed the bit off in the desired direction. There were several drawbacks with this tool. The bit used to kick off the hole was always smaller than the required hole and drilled a pilot hole which had to be enlarged. The whipstock had to be pulled out of the hole and reset every 25 ft or so, after the pilot hole was opened out, in order to achieve sufficient angle build-up.

The modern method of kicking off a directional well is to use a down-hole motor or a turbodrill and a 'bent sub'. The string consists of a full gauge bit, turbodrill, bent sub, non-magnetic drill collar, drill collars, and drill pipe. The bent sub, or angle sub, is a short piece of drill collar on which the axis of the pin is at an angle relative to the axis of the box. The angle is small, ranging from $\frac{1}{2}^\circ$ to 3°. The non-magnetic drill collar is used to provide a seat for the magnetic survey instruments which are run to survey the hole. Before kick-off the turbodrill assembly is run to the bottom of the hole and a survey is taken, the

instruments being run into the drill string on a wire line or the sandline. The survey instruments consist of a plumb-bob and a compass which show the inclination and direction of the drill string at the non-magnetic collar. They are both contained within a pressure-tight case, and when seated in the collar a time-actuated camera photographs their readings. Upon retrieval from the hole the film is rapidly developed and their readings are obtained. The kick-off string is then orientated and the mud circulation started. The turbine drives the bit with the remainder of the string restrained from rotating to maintain the direction, while building angle. The rate of building up depends on the formation and the angle of the angle sub employed, but $2\frac{1}{2}^{\circ}$ to 3°/100 ft is reasonable.

An alternative method of kicking off uses a steering tool. A similar string to the above is used, except that the non-magnetic drill collar is replaced by a special landing collar or sub for a gyroscopic measuring instrument. This can measure the hole angle and direction, and the direction in which the drilling tool is heading. This information is passed back to surface, either through a wireline or as pressure pulses through the drilling mud system, and the orientation of the drill string and bit weight are altered as necessary to get the required hole direction and angle build-up.

Drilling with the motor or turbodrill continues until an adequate angle build-up is obtained, a survey being taken every 30 to 60 ft. The turbodrill is then pulled out of the hole and a rotary drilling string is run to continue drilling. By using various combinations of weight and rotary speed, and by changing the position of stabilizers in the drill collar string, to increase or decrease their pendulum effect, the hole can be made to build, maintain or lose angle or to change direction. This is part of the art of directional drilling, and one or two wells in any area have to be drilled before the effects of various drilling assemblies can be forecast. The degree of control required on a directional hole varies from place to place, depending on the nature of the formation being drilled, its dip, etc., and it is a case of trial and error to discover the best assemblies to use.

The hole is surveyed frequently (every 30 to 60 ft) during angle build-up, but once the course is established the interval is increased to 200 to 300 ft. A plot of the track of the hole is kept, showing the horizontal and vertical section, to ensure that it is staying on course.

Directional drilling is also used to sidetrack a fish left in the hole, or to straighten a vertical hole that has been deflected by steeply-dipping beds.

Turbodrills

In recent years much research has been directed towards finding better ways to drill holes in the earth, basically avoiding rotation of a long slim drilling column and its removal from the hole when the cutting tool is worn out.

Avoiding rotation has partly been resolved by the advent of the turbodrill. Pioneered in Russia, it is now a popular drilling tool in Europe, where its high speed of rotation (600–1000 rev/min) makes it the ideal partner for the diamond bit in firm to hard formations.

There are two types of down-hole mud motor: the turbine, of which there are about three successful types, and the Dynadrill/Navidrill type, a Moyno pump

operating in reverse, consisting of a spiral shaft contained within a rubber sleeve. Drilling mud forced between the rubber sleeve and the shaft causes the shaft to rotate.

The down-hole turbine is basically similar to a gas turbine having a multistage stator and rotor. For directional drilling kick-off work they are kept fairly short, about 25 ft, and have 50 to 60 stages. For continuous drilling they have been lengthened to 40 ft, and contain up to 150 stages. Normally it is not economic to use a turbodrill with a tri-cone bit, because of the rapid wear caused by the high rotational speeds. For drilling long continuous sections of firm to hard formation, the turbodrill/diamond bit combination has proved highly successful, the assembly staying in the hole for well over 100 hr and outdrilling rotary tools. It has also proved very useful in drilling through formations where it is undesirable to rotate the drill string too fast, in case of drill-pipe failure, for example in hard rock below a washed-out formation, where the harmonics in the string would cause premature failure through excessive fatigue.

When using a turbodrill the mud must be kept in good condition and free of sand or any other abrasive particles.

To date, the largest size hole regularly drilled with the turbodrill is $12\frac{1}{4}$ inches, but directional wells are regularly kicked-off with both 26-in and $17\frac{1}{2}$-in bits driven by short directional turbodrills. Under special conditions down-hole mud motors of the Dynadrill/Navidrill type are used to drill 26-in and 17-in hole driving regular tri-cone bits.

Well Surveying

When drilling a well it is important to know fairly accurately its depth and position relative to the surface location. The depth is easily obtained when the hole is vertical, since every item in the string is carefully measured before going into the hole, and a running total is maintained as each joint of drill pipe is added.

A truly vertical hole is impossible to drill, but an inclination of less than 5° to the vertical is generally acceptable. The inclination of a vertical well is usually checked each time the drill string is pulled to change the bit. An inclinometer in a robust, pressure-tight case, is dropped inside the drill string and lands in the drill collar just above the bit. After a pre-set time a delayed-action mechanism records the inclination by pressing a small target chart against the pointer of a plumb-bob device. The instrument is recovered when the bit is unscrewed from the bottom drill collar.

This instrument measures inclination only and is basically used to check for any major changes in the angle of the hole.

If the angle and direction of the hole are continuously required then it would have to be treated as a directional well and a non-magnetic drill collar would be run in the string above the bit. The well could then be surveyed at regular intervals as described in the section on directional drilling. On completion of the well the inclination and direction can be checked by running a multi-shot survey instrument, either magnetic or gyroscopic.

The magnetic survey instrument is dropped into a non-magnetic drill collar, recording as the string is pulled out. The gyroscopic survey is carried out in the

cased hole, the tool being run on a wireline. In each case the survey is recorded on a continuous film at a fixed time-interval, usually every 20 sec, as the instrument moves up the hole. The results are plotted to give horizontal and vertical pictures of the path of the hole.

Measurement While Drilling(MWD)

The latest developments in surveying tools are incorporated in Measurement While Drilling (MWD) equipment. These tools are run as part of the drilling assembly. In the case of surveying (Teleco) each time a survey is required, drilling is halted, the bit picked up off bottom and circulation continued. The survey sequence occupies approximately $1\frac{1}{2}$ minutes after which data are transmitted to the surface as pressure pulses superimposed upon the circulating mud pressure. If the drill string is not rotated, as when kicking off a directional hole with a turbodrill and bent sub-assembly, the Teleco system collects and transmits data continuously. A new set of readings is sent to the surface about every $2\frac{1}{2}$ minutes.

Other systems are being developed which will continuously transmit information on temperature, weight on bit, mud pressure and flow rate at bit, and gamma radiation and resistivity of the formations as drilled.

Electric Logging

As the successive casing depths are reached, the open hole is logged before casing is run and cemented. Electric, sonic, and radioactive logging tools are run into the hole on a multi-core cable, from the winch of a special self-contained logging unit. The cable is accurately calibrated to record depth.

The logging tool is run to the bottom of the hole and the log is recorded as it is pulled out. The returning signal from the tool is recorded photographically on a continuous film strip, which facilitates reproduction. The use of the multi-core cable allows two or three different logs to be recorded at the same time, for example a caliper of the hole and a sonic log.

The sonic logs record the difference in transit time of a sonic pulse through the formation adjacent to the tool, the electric logs record the resistivity of the formations, and the radioactive-logging tools measure the natural radioactivity of the formations and also that induced by running a radioactive source past them. From this information it is possible to deduce the porosity, fluid resistivity, and fluid saturation of a formation, and to determine changes in lithology for geological correlation purposes.

The logging line is used for running the cement bond log, which measures the bonding between casing and cement, and cement and formation, and the dip-meter, which measures formation dips. Continuous directional and deviation surveys can also be run. The logging cable is also used to run and fire explosive devices for perforating casing.

Coring

During the drilling of a well the taking of a core is often required, particularly in the reservoir rock of the pay zone. A core is an undisturbed sample of the

formation required by the geologist and palaeontologist for correlation and identification purposes, and by the reservoir engineer for permeability and porosity studies, and for oil and water saturation measurements. Cores are usually taken on exploration wells and early development wells.

Cores are taken with a core barrel, which consists of an outer and inner barrel. The outer barrel is a case which acts as protection for a thinner-walled inner tube. The two are connected by means of a bearing at the top of the inner tube which, to avoid damage to the core, does not rotate. Circulation is through the annulus between the two. A core bit is attached to the bottom of the outer barrel. Core heads are usually diamond, similar in design to a diamond bit, but with a concentric hole through the face, the diameter of which is fractionally smaller than the inside diameter of the inner barrel. When the core barrel is rotated on the bottom the uncut section of the formation passes through the centre of the bit and into the inner barrel where it is held by catchers. On completion of the core, the string is pulled from the hole, the inner barrel is removed, and the core is extracted hydraulically with a hand pump.

The procedure for taking a core is basically the same as for ordinary drilling, except that the weight and rotary speed are much more carefully controlled to ensure that the outer barrel will not buckle and break the core. Core barrels are made in multiples of 30 ft and, depending on the type of formation, up to 60 ft of core can be cut in one run of a two-section barrel.

A special barrel is available for coring loose, friable formation such as poorly-cemented sandstone. The inner barrel contains a rubber sleeve which envelops the core and stops it falling apart during the coring operation, thus allowing it to be removed in one piece.

DRILLING FLUIDS

When dealing with the drilling fluid circulation system, mention was made of provision at the well for storing, testing, conditioning and treating this fluid, and its use for the removal of cuttings, sand and other drilled debris. In some developing fields, centralized mud treatment and recovery plants are employed for storage, batch preparation and reconditioning of the fluid, and for the recovery of weighting additives. The reconditioned drilling fluid is conveyed to the well by tank-truck or pipeline. Special supply ships are used for transporting drilling fluid and drilling-fluid materials to platforms and barges on offshore locations. Helicopters are used to transport drilling-fluid materials to remote land locations.

Water-base drilling fluids generally fulfil the requirements for drilling oil wells. However, the use of more expensive oil-base or water-in-oil emulsion is demanded by certain down-hole conditions. Similarly, air or aerated drilling fluid has specialized application as a circulatory system.

The major functions of the drilling fluid are:

1. To cool and lubricate the drilling bit and the drill string.
2. To remove drilled solids, allowing their release at the surface.
3. To form a gel to suspend drilled cuttings, and any weighting material, when the fluid column is static.
4. To control subsurface pressures.

5. To prevent squeezing or caving of formations and to plaster the sides of the borehole.
6. To minimize damage to any potential production zone.

In order to assess the quality of the drilling fluid and ensure that it is properly conditioned to carry out the desired functions, its properties are evaluated regularly in accordance with standard API testing procedures. The most important of these properties are density, viscosity and gelation characteristics, filtration rate, filtrate chemical composition, pH value, sand and solids concentration, and emulsion stability. Generally speaking the principles involved in the control of drilling fluid properties are associated with the study of the physico-chemical behaviour of clay suspensions.

Cooling and lubrication of the bit are simple but essential duties. Great heat is generated when drilling, and this is dissipated by the circulating fluid, otherwise the bit would burn out. Improved lubricity by addition of oil and special proprietary additives can contribute to longer bit life and increased rate of penetration.

The fluid velocity in the annulus between drill string and borehole, the density and the viscosity of the drilling fluid, influence its efficiency in lifting cuttings. The circulatory pump performance plays an important part, the hydraulics of the drilling fluid being closely related to the flow or rheological aspects of the system. By consideration of these flow characteristics, the dimensions of the drill string and the size of its restrictions, such as bit nozzles, pressures can be pre-determined for optimum circulation rates, and appropriate size liners can be installed in the pumps. The density of the system governs the buoyancy factor in lifting cuttings, whilst the viscosity, or flow characteristics, can be adjusted to improve carrying capacity. Measurements of viscosity characteristics take into consideration the fact that drilling fluids are not true fluids (Newtonian), but are suspensions of solids in liquid that obey the laws of plastic flow. With such systems, viscosity values change with rate of shear, and apparent viscosity characteristics are measured under conditions of constant rate of shear. True flow characteristics are defined by plastic viscosity, which is a measure of resistance to flow due to size, shape and number of particles, and yield point which is a measure of resistance to flow due to forces existing between particles.

Dilution with water can control drilling fluid viscosity. However, when this method is not applicable, chemical viscosity-reducing agents or thinners such as sodium polyphosphates, tannins, lignins, lignites, and lignosulphonates can be used, as required by circumstances. For optimum thinning capacity most thinners are used in conjunction with caustic soda, since viscosity control is also a function of the pH value. At elevated temperatures lignosulphonates degrade and become ineffective. Where temperatures in excess of 180 °C are expected more specialized dispersants, frequently based on sulphonated styrene/maleic acid copolymers, are used. These materials are more expensive than the conventional thinners, but they enable water-based fluids to be used to greater depth and thereby avoid the increased cost of converting to oil-based muds. The inclusion of special de-silting equipment also assists in viscosity reduction by mechanical rejection of dispersed drilled solids.

Gelation, which is a measure of the attraction of drilling fluid particles for

each other, indicates the thixotropic characteristics imparted by gel-forming clay materials and their physico-chemical adjustment, thixotropy being the comparison of gel strength measured initially and after a prescribed period of quiescence. This property of forming a gel when quiescent but developing fluidity on subsequent agitation, is a most important characteristic of drilling fluids, governing suspension properties and the release of drilled cuttings and gas at the surface.

Pressures associated with subsurface gas, oil, or water can be controlled by increasing the specific gravity of the fluid, and therefore the hydrostatic head of the drilling fluid column. A weighting material, barytes or barium sulphate, ground to specified particle size and prepared according to other standard requirements for use in drilling fluids, is the most common material used for this purpose.

Because a positive pressure differential usually exists between the column of drilling fluid and the formation, there is always a tendency for the fluid phase to enter any permeable zone. Generally formation permeability is too low to permit the entry of mud solids, and these are left adhering to the borehole wall as filter cake.

Some filtration is usually acceptable, and indeed the plastering effect of the solids is frequently beneficial in maintaining the integrity of the borehole wall. However, excess filtration of the fluid must be avoided and specific additives—starch, sodium carboxymethyl-cellulose, and sodium acrylate—are available to control the extent of filtration.

Certain shales are particularly sensitive to water and are liable to hydrate and slough into the borehole if contacted by fresh water. Hydration can be impeded by the presence of certain ions—potassium, calcium, or ammonium, for example—in the system. Sloughing and squeezing of sensitive formations may sometimes also be prevented by increasing the weight of the fluid and thereby 'propping-up' the borehole wall.

Production zones can contain water-sensitive clays, and the intrusion of water filtrate from the drilling fluid results in hydration and swelling of clay, with consequent reduction in the porosity and permeability of the reservoir. Solids suspended in the drilling fluid can also block the formation near the well bore owing to differential pressure exerted by the drilling fluid against the formation, if this differential is not strictly limited to values commensurate with safe drilling practices. This impairment of productivity is usually referred to as formation damage. Sometimes oil-base drilling fluids or water-in-oil emulsions are used to avoid the damaging influence on well production by aqueous filtrate.

To drill rock salt, the drilling fluid is saturated with salt to avoid leaching the formation, which could cause enlarged hole development and consequent collapse of any interbedded formations. Special salt-water clays are used to obtain satisfactory viscosity/gelation characteristics, with organic additives, mentioned earlier, used for filtration control.

For offshore locations, sea water is used for drilling-fluid preparation, and appropriate chemical conditioning agents are added to offset the deleterious effects that brine could have upon good drilling fluid properties.

Salt, anhydrite, and gypsum flocculate ordinary types of drilling fluid and destroy their desirable colloidal properties. Contamination by salt from salt

formations or high-pressure brine shows can be countered, either by conversion to salt-saturated drilling fluid, or by special chemical treatments similar to those used in the preparation of sea-water muds. If anhydrite- and gypsum-bearing formations are penetrated, chemicals, for example, sodium carbonate, are added to the drilling fluid system to remove contaminating calcium from solution. However, modern drilling-fluid systems conditioned with lignosulphonate dispersants need only minor corrective treatment. Cement left in the borehole after cementation operations may contaminate the drilling fluid, and sodium bicarbonate is used as a corrective measure.

If drilling fluid is lost to porous or fractured formations and reduction of density by conventional methods is not an effective control, suitable sealing agents such as cellulose, mica, wood and vegetable fibres, and groundnut shells, are added to counter the loss. Cement mixtures are used to seal off formations in some circumstances. The ultimate resort for negotiating zones of loss, if other methods have failed, is the use of aerated drilling fluid or air to reduce hydrostatic head. Drilling with no returns to surface using water, referred to as blind drilling, is used in the most severe conditions of lost circulation, where unlimited supplies of water are available.

Classification of Drilling Fluids

Water-based drilling fluids

1. Fresh water
2. Brackish or sea water
3. Salt-saturated
4. Calcium (a) lime-treated; (b) gypsum
5. Inhibited
6. Surfactant
7. Low solids
8. Polymer
9. Aerated.

1. *Fresh water.* The liquid phase contains only small amounts of dissolved salts and is conditioned by a proprietary grade of standard bentonite clay. Drilling fluids controlled by addition of tannin thinner are often called red muds, because of the red colour imparted by this particular additive. They can be sub-classified into low pH and high pH red muds, depending upon the amount of caustic soda added in conjunction with the tannin. These red muds effect good dispersion of solids if formations penetrated have poor mud-making qualities. With high pH systems, pre-gelatinized starch can be added to improve filtration characteristics without preservative for starch protection.

2. *Brackish or sea water.* Drilling fluids used at offshore locations involve special salt-water clay (attapulgite or sepiolite) additions to achieve desirable suspension characteristics, with the organic derivatives (sodium carboxymethyl-cellulose or pre-gelatinized starch) added to correct high filtration values. Bentonite will not hydrate in salt water. If conditions dictate its use the clay must be pre-hydrated in fresh water at high concentration and then diluted to the required level with sea water. Starch or CMC can be used for

filtration control. Since salt water has a corrosive effect on drilling tubulars, inhibitors are sometimes required.

3. *Salt-saturated.* Special salt-water clay (see above) is also used in the preparation of this type of drilling fluid. Since these systems have very little response to thinning by chemical means, viscosity control is generally carried out by dilution methods, together with mechanical means (de-silters) for rejection of drilled solids.

4. *Calcium.* These systems depend upon the influence of calcium ion absorption on clay particles to produce low-viscosity, low gel-strength conditions. They withstand the contaminating effects of cement, anhydrite and salt, when the drilling fluid is properly conditioned. Organic additives are employed for filtration control.

(a) Lime-treated: hydrated lime is used as the source of calcium, but the systems have a disadvantage in that they tend to solidify at high temperatures, i.e. 120°C+; hence their limited use in very deep holes.

(b) Gypsum: gypsum is the source of calcium and the special dispersant, ferrochrome lignosulphonate, is used. Gypsum-treated drilling fluids are less alkaline than lime muds and are not so susceptible to high-temperature solidification.

5. *Inhibited.* Generally used for shale control, these drilling fluids are inhibitive to hydration and swelling, and also to damage of producing zones containing water-sensitive clays. Salt, lime, gypsum, sodium silicate, and a combination of chrome lignite/chrome lignosulphonate dispersants can be used in the achievement of their special characteristics. Certain long chain polymers, e.g. polyacrylamides, tend to adsorb on to the surface of active shales and further inhibit their dispersion. This mechanism is generally known as 'encapsulation'.

6. *Surfactant.* These drilling fluids have been treated with surface-active agents to reduce interfacial tension between surfaces of drilling fluid ingredients for reduction of viscosity, to control filtration characteristics and the tendency to water block in producing zones.

7. *Low solids.* These are low-density drilling fluids, carrying the minimum amount of solids (not exceeding 10 per cent by weight) relative to safe drilling practices. Because of their low solids content, they can contribute appreciably to increased rate of penetration. Density is kept low by adequate rejection of drilled solids and/or addition of oil to obtain oil-in-water emulsion and, in the absence of clay, any viscosity increase adjustments can be made by use of viscosity-boosting organic additives.

8. *Polymer.* Certain special polymer compounds are added to obtain rheological control to allow low viscosity at high rates of shear (i.e. through drilling bit nozzles), thus promoting increased rate of penetration. On returning to surface up the annulus, the drilling fluid thickens to provide comparatively good cuttings-removal capacity. It is essential that as far as possible all the drilled cuttings are removed by the surface equipment. Once the solids content of a polymer mud has built up chemical dispersion is required, and the advantage of a polymer fluid is lost.

9. *Aerated.* When compressed air is added to the drilling-fluid column to reduce hydrostatic pressure, chemicals have to be added to protect against corrosion (oxygen cell).

If conditions allow (no water-bearing formations exposed) compressed air alone can be used. If water ingress is strictly limited, foam or mist systems are created.

The above water-base drilling fluids are often emulsified (oil-in-water emulsion) by adding oil. Volumes of oil up to 15 per cent can be added and the various additives in the drilling fluid act as emulsifiers. Volumes in excess of this are accompanied by the addition of secondary emulsifiers.

Oil-based drilling fluids

1. Oil-base
2. Water-in-oil emulsion.

1. *Oil-base.* Oil-base drilling fluids vary mainly in the means of maintaining control. In most cases, blown asphalt materials furnish a means of controlling filtration, whilst metallic alkali soaps develop necessary gel strength for suspension characteristics. They usually have 1–5 per cent by volume of water dispersed in the oil. Diesel oil is generally used as the base for most oil muds. However, many regulatory authorities are becoming concerned at the discharge of cuttings coated in diesel oil, and steps have to be taken to remove the oil from the cuttings before disposing of them. Cuttings, therefore, have to be washed in surfactant or incinerated prior to discharge, or alternatively an oil mud prepared from an oil low in aromatic content has to be used.

2. *Water-in-oil emulsion.* By contrast with actual oil-base drilling fluids, water-in-oil emulsions can contain up to 50 per cent by volume of water as the dispersed phase. To obtain stability, emulsifiers and stabilizers are added, with oleophilic clays contributing the gelation properties. Special proprietary additives are available for viscosity control.

WELL COMPLETION

Casing

Casing is the thin-walled steel pipe used to line the borehole. It is manufactured to American Petroleum Institute standards, which specify the grade of steel to maintain the minimum wall thickness, the outside diameter, the wt/ft and some, but not all, of the threaded connections used.

Casing specifications differ from those of all other line pipe in that, for the convenience of rig crews, the outside diameter is the only stated dimension. As the driller must always work within the lifting capacity of the rig, the wt/ft as a measure of wall thickness is also given.

To maintain minimum wall thickness, casing is manufactured from grades of steel having ultimate yield strengths in the range 40 000 to 150 000 lb/in^2.

Wells drilled for oil or gas production are lined with several strings of casing for the following basic reasons:

1. To prevent caving of the borehole.
2. To prevent contamination of potable water reservoirs.
3. To provide anchorage for the wellhead and blowout preventers.
4. To exclude water from the producing formations.
5. To confine production to the borehole.
6. To provide an adequate means of controlling well pressures.

Most of these reasons apply to the drilling phase of the well so that casing strings are not run specifically for production purposes.

A completed well could have as many as five strings of casing set, depending upon the depth of the hole and the formations and problems encountered. Most wells are cased through the production zone or zones, and the casing is perforated as necessary. Some, however, are completed barefoot, which means that the last string of casing is cemented into an impermeable cap rock above the production zone and the hole drilled into the pay zone is left uncased. For this to work successfully the pay zone must be dolomite, limestone or a competent silt or shale.

Selection of a well-casing programme generally depends on whether the well is for exploration or production. If it is an exploration well and coring, drill-stem testing, and extensive logging are planned, then it is desirable to get as big a hole as possible, as deep as possible. This means starting with a large casing size at the top of the hole and ensuring that the last string run before entering the deepest potential pay zone will allow the use of standard logging tools, test tools and core barrels. It must also be capable of containing the closed-in pressure of any fluid encountered and the pressure involved in any stimulation operation such as hydraulic fracturing or acidization.

By their very nature, exploration wells are dealing with the unknown, so high design factors on casing burst and collapse are usually employed.

Casing-programme design for development wells is governed by the final completion of the well, whether it is a single- or multi-zone completion, casing or tubing completion, natural flow or artificial lift, or even oil or gas completion.

In practical terms there are about three standard combinations of casing-string sizes, and all the tools and equipment for these combinations are standard stock items. It is thus more economic to design to these standard sizes.

As the highest radial stresses in a casing string occur at the ends, collapse occurs at the bottom, burst at the top, and the maximum tensile loading at the top, it is common practice to run composite casing strings containing casing of different weights and grades. The heavier or higher-grade pipe will be at the top and the bottom, and the lighter or lower-grade pipe will be in the middle.

In the event of what would normally be the final casing string being run before the pay zone is reached, or if it is not necessary for the final casing string to be run to surface, a liner is used. This is a casing string which stretches from the bottom of the hole to just inside the bottom of the last casing string. It is cemented into position and is hung on a special hanger which seals off the annulus against the previous casing string.

Cement

When casing is run to the required depth in a well, it is cemented into position. This is done by mixing and pumping into the casing sufficient cement slurry to fill the annulus between the casing and the open hole, and the casing and the previous casing. The cement is then displaced into the annulus by pumping drilling mud into the casing. The mud and cement are separated by rubber spacers or plugs (Fig. 10.).

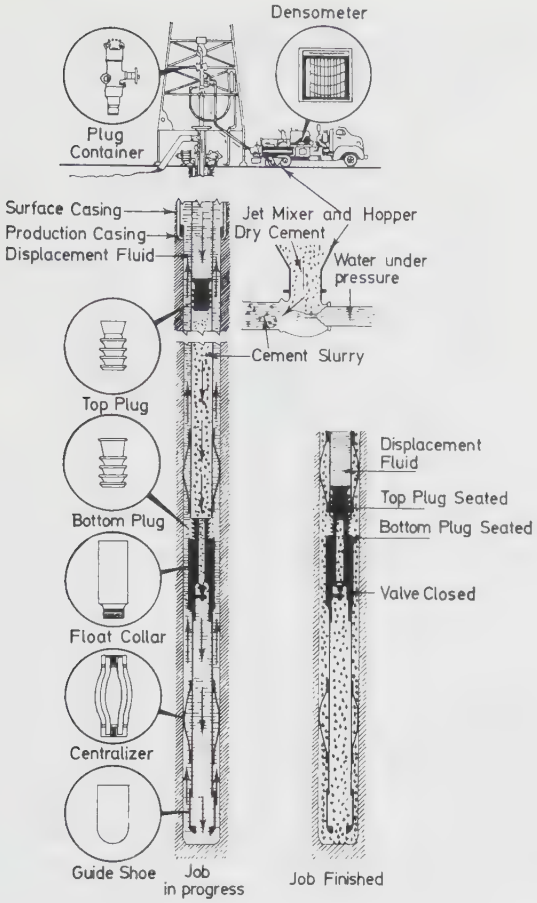


FIG. 10. Diagram of primary cementation.

The cement supports the casing, seals off the annulus, isolates porous zones from each other, and protects the casing from corrosive formation fluids.

Cements for use in oil or gas wells are manufactured and classified in relation to the ultimate depths to which they are to be pumped. Using samples of the mixing water available at the drilling site, such as saline or sea water, slurry mixtures are tested in the laboratory. Their pumpability, compressive strength and other characteristics are determined by means of standard apparatus and procedures, which simulate the temperature and pressure regimes experienced by the cement in the borehole. If special conditions exist, such as long salt sections in the well, salt would be added to saturate the water.

Oil-well grades of cement are nearly all sulphate-resistant, since water containing sulphates has a deleterious effect on set cement. Because the cement slurries have to be pumped considerable distances, often at elevated temperatures, the setting process may have to be retarded. Lignins or citrates, either as powder or in liquid form, are the basis of most proprietary retarders.

Conversely, surface holes in many parts of the world are at very low temperature, requiring an accelerating agent (calcium chloride or sodium chloride) in the cement.

The slurry performance and success of a cementation depend upon maintaining an optimum water/cement ratio. Therefore, during cementation the slurry density is measured continuously or at frequent intervals. Sometimes a slurry density higher or lower than that of neat cement is required, necessitating a change in the water/cement ratio. To facilitate this change various additives have to be used. To lighten the slurry a special grade of diatomaceous earth is used, which works by means of its own low density and by permitting larger additions of water. To increase the slurry density, high specific gravity additives are used, the principal one being ilmenite, an iron-titanium oxide, which increases the average density of the solids and effectively reduces the amount of mixing water.

Poor casing cementation is usually the result of a failure to remove all of the mud when the cement is displaced into the annulus. Cementation programmes are designed to obtain a slurry flow pattern that assists in the improvement of mud displacement. This involves:

(a) Using friction-reducing additives in the cement and displacing the slurry at a sufficiently high pumping rate to obtain turbulence, an acid wash being pumped ahead of the slurry.
(b) Displacing the cement slowly so as to achieve plug flow and preceding it with an acid wash.

Considerable discussion is in progress as to which of these is the most effective, both having been successful.

The quality of a casing cementation can be assessed by the use of the cement bond log, which is run by the logging unit. This utilizes the difference in transmission strength of a sound wave through bonded and unbonded casing. On evidence from the cement bond log, remedial cementation can be carried out, if necessary, through perforations in the casing.

Wellhead and Fittings

Natural flow wells

The only visible part of an oil or gas well consists of the wellhead, which is basically the casing head housing, casing and tubing head spools, and the production valves and chokes, collectively called the Christmas Tree.

The casing with which the well is lined is hung on or landed in the wellhead (Fig. 11). The surface casing is screwed into the bottom of the casing head housing, which is the lowermost part. It is a short forged-steel cylinder, the bottom screwed to match the casing, the top flanged and with smaller side outlet flanges or flanged connections. Inside the top of the housing is a tapered bowl in which the next string of casing is landed in a wrap-around slip assembly incorporating a rubber seal. Subsequent casing strings are landed in casing head spools, which are similar to the housing, but have flanges at each end. The wellhead is built up as the well is deepened, additional spools being added as each casing string is run. The smaller side connections of the spools are

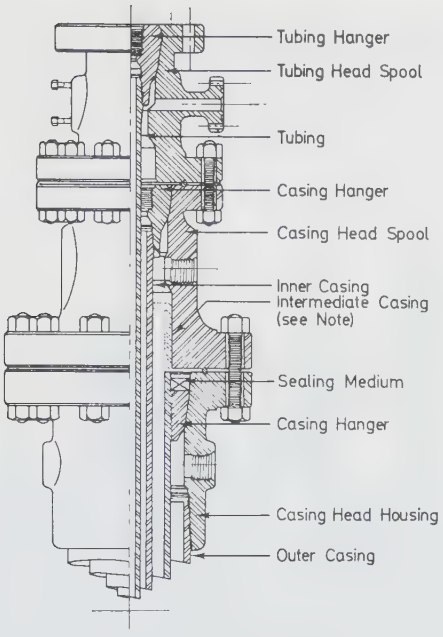


Fig. 11. Wellhead diagram.

either blanked off, or fitted with a valve and blank flange. During drilling the blowout preventers are bolted to the top flange of each spool in turn. The side connections allow access to the well below the preventers while drilling, and to the annulus between any two casing strings after casing is set.

The tubing head spool from which the production tubing is hung is the topmost spool on the wellhead, and is basically similar to a casing head spool. Radial hold-down screws are incorporated in the top flange to hold the tubing hanger in position. If the well produces via tubing and annulus, the annulus production is taken off through the side arm valves of the tubing head spool.

The production valves and chokes at the wellhead are bolted to the top of the tubing spool. The size, number, configuration, and pressure rating vary considerably from field to field. Some have separate valves bolted together, some have all the valves let into one block of steel, and others have a mixture of the two. A typical production wellhead and Christmas Tree are shown in Fig. 12; it costs approximately £100 000.

Pumping wells

The wellhead on a pumping well is a much simpler arrangement, as the wells are usually shallow and there are no high-pressure problems. The tubing is landed in a housing screwed to the last casing string, on top of which is bolted or screwed a tee-piece and stuffing box. The top section of the sucker rods is polished to pass through the gland of the stuffing box. As the sucker rod string rises and falls, oil is lifted from the well and flows out through the side arm of the tee-piece through a valve.

Cameron Iron Works Ltd.

FIG. 12. Typical high-pressure wellhead and Christmas Tree.

Production wells

Having drilled the well into the production zone and run and cemented the final casing string, it is then necessary to complete the well for production. The type of completion, the number of strings of tubing, their size, the safety devices incorporated in the well vary considerably from field to field. They are governed by the nature and productivity of the pay zone, the number of pay zones, surface environment, and local legal requirements.

In some areas, where the pay zone is very permeable or fractured, the well can be killed by pumping the oil back into the formation and filling the hole with mud. This type of well is usually a barefoot completion, but can be produced via perforations in the oil string casing and merely capped by the production valves or Christmas Tree. The well is induced to flow, if necessary, by pumping water into the casing and squeezing away mud to the formation.

The reduction in pressure head in the casing after sufficient mud has been replaced by water, is sufficient to start the well flowing. These wells are usually big producers, e.g. 5–10 000 tons/day in Gachsaran, Iran.

Where the pay zone is insufficiently permeable, or is susceptible to damage from the drilling, a tubing string is hung from the wellhead to near the bottom of the well. Heavy mud can be circulated down this 'kill string' and into the annulus to kill the well. Oil may be produced from both annulus and tubing or one or the other depending upon the local requirements. The well is brought in by circulating out the drilling mud with a lighter fluid, such as water or gas oil.

In some areas where the wells are not easily accessible, i.e. offshore, a packer is run on the tubing and set just above the pay zone. Completion fluid of high enough density to kill the well is contained in the annulus above the packer and production is via the tubing. Also in the tubing string are special short lengths of pipe known as landing nipples. These have internal recesses machined into them, into which special tools are run and located, on wireline. The nipples are usually placed near the bottom of the tubing and are used to locate such things as bottom-hole chokes, pressure gauges during surveys and down-hole safety valves. Many other wireline tools exist, their use being dependent on the type of completion in question.

In some wells utilizing a tubing string for production, a safety valve, controlled hydraulically through a hose from the surface, is incorporated in the string fairly near the surface. If the tubing is a simple kill string and production is via both annulus and tubing, the safety valve will be incorporated in a packer through which both streams will flow. In the event of an accident or mishap dropping the pressure on the control line, the valve will close, shutting off the flow of oil in both cases.

Several different pay zones in a well, at different pressures, can be produced separately by running more than one string of tubing and isolating each zone between packers; for example, if three zones exist, three tubing strings can be run and triple-, dual- and single-bore packers used. The disadvantage with this type of completion is that as the number of tubing strings is increased, their size gets smaller, thereby restricting their productivity. To overcome this, tubingless or permanent completions have been used. Instead of running the final or oil string casing, two, three or even four strings of tubing are run into the open hole and cemented in position. Each string is then perforated opposite one or more zones and produced separately. The tubing in a multi-permanent completion can obviously be bigger than the equivalent number run inside casing.

In the event of the gas/oil ratio of the crude oil being so low that it will not flow, a completion incorporating some form of pump has to be used. Generally these wells are fairly shallow, 1000–4000 ft, and it is possible to run an electrically operated pump into the bottom of the well. However, the most common method is the down-hole plunger pump connected by sucker rods to a walking beam at the surface. The walking beam imparts a reciprocating motion to the pump, which lifts the oil to surface.

Stimulation

After a completed well has been on stream for a short time, it may be found that the production rate is below that expected. This could be caused by low

permeability of the formation or invasion by the drilling fluid. There are many ways of cleaning up and stimulating a well, the main ones being acidization and hydraulic fracturing.

Acidization is used to stimulate reservoirs consisting of limestone and dolomite, which are acid-soluble. Hydrochloric acid is generally used, mixed with an inhibitor to protect production tubing and casing. The acid is circulated or pumped to the bottom of the well, squeezed into the production zone and left in place for a short period, before back-flowing. The acid opens up and enlarges channels and fissures in the reservoir rock around the borehole, by dissolving the formation.

Hydrofluoric acid is used to stimulate sandstone reservoirs where the sand grains are bound together by a non-calcareous matrix. The matrix is dissolved and opens up channels assisting the flow of oil or gas. In some cases it is also used to dissolve clay solids that have invaded the sandstone from the drilling mud.

Hydraulic fracturing or hydrofraccing, is a method of opening up fissures and cracks in the pay zone around the borehole. The pressure required to break down the formation and extend the cracks varies from field to field but is usually between 65 and 85 per cent of the overburden pressure.

Having broken down the formation and extended the fracturing some way from the borehole, propping agents must be used to keep the fissures open once pressure is released. These are carried by the fracturing fluid, which is usually a gel, and consist of coarse rounded sand, walnut hulls, glass beads, etc., depending on the nature of the formation.

Fracturing can be carried out through the production tubing, particularly if a packer is set above the pay zone, and the complete zone can be treated at one time. However, if selective fracturing is required it is often necessary to pull the tubing and run a special fracturing string with isolating packers, etc.

Very high pressures, 6–8000 lb/in^2, are often involved when hydrofraccing, necessitating stringent safety precautions and a high standard of competence from the personnel involved.

Drilling Costs

The cost of oil and gas well drilling varies considerably from well to well. It depends on the depth, the type of well, the location, whether offshore or onshore, the hole problems involved, and many other considerations.

On land, one of the most important is the geographical location of the well. If the rig has to be specially modified to cope with the environment, such as the North Slope of Alaska or the remote jungle of Peru or Colombia, then extra expense is involved in mobilizing, rigging up, and operating the rig. Support costs in this type of location, which invariably involves the use of aircraft, can account for more than half the total cost.

Typical costs for onshore drilling rigs are:

Mobilization	£500 000
Rig hire	£10 000/day with camp
Rig hire	£6 000/day without camp

All-in operating rate which includes all support costs, fuel, transport, etc.—£18 000 £25 000/day.

Offshore drilling operations are more expensive than onshore because of the very high initial cost of the drilling platform or mobile offshore unit. Typical costs are:

Fixed platforms vary from £50 million to £500 million, depending upon the water depth and location.

Platform rig hire: £8 000–£10 000/day

Jack-up unit—mobilization up to £2 million dependent upon distance.

Rig hire: £25 000/day

Semi-submersible and drill ship.

Mobilization	£2 million–£3 million
Rig hire	£35 000–£45 000/day
Supply boats	£4 000–£4 500/day
Helicopters	£2 500–£3 000/day

All-in operating rates.

Jack-up unit	£45 000/day
Semi-sub/drill ship	£70 000–£90 000/day

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5

Reservoir Engineering

By C. J. MAY

INTRODUCTION

The conditions under which crude petroleum and natural gas occur in nature have been outlined in earlier chapters together with a discussion of the methods used in finding the various local accumulations or reservoirs. Normally, absolute proof of the presence of hydrocarbons can only be obtained by drilling wells, which also provide the only outlet, and practically the whole of the current petroleum production is derived in this way.

Ultimately the world's commercial hydrocarbon reserves will be greatly increased by the mining of tar sands and the distillation of oil shales; the first commercial-scale plant exploiting the Athabasca tar sands of Northern Alberta is in fact now in operation, and the production of shale oil on a modest scale has a long history in various countries. However, at present these methods are only of limited significance and no more than brief reference will be made to them in this chapter.

The problems arising in the course of production from the conventional type of field are broadly speaking of two kinds. First, there are the mechanical difficulties involved in the drilling of wells to obtain access to the producing formation and in lifting the oil to surface; so far as these are concerned, the practical methods available are not dissimilar in principle to those used in the production of underground water, though there are many complications in detail due to generally greater depth and higher pressure.

Secondly, various specific and important problems arise from the fact that oil is always intimately associated with gas and water, and at the same time the amount in any particular reservoir is limited. Removal of oil leads necessarily to a reduction in pressure and a redistribution of the reservoir fluids; in consequence, the practicable rate of production declines with time until continued operation becomes unprofitable, even though only a fraction of the oil originally in place has been recovered. The recovery actually achieved from a given reservoir is dependent partly on the natural conditions and partly on the design and control of the producing operation.

A considerable effort to achieve a high percentage extraction of oil is commonly justified by the very large capital expenditure involved in the discovery and development of a new field, but refinements in operating techniques can be expensive and beyond a certain point yield diminishing returns. Hence there is no unique value for the producible reserves of a particular field; the amount of oil obtained in practice is dependent on a complicated balance of technical and economic factors.

Some oil can always be extracted by random drilling and rule of thumb methods of production, and where natural conditions are favourable the percentage recovery by such methods may be fairly high. In general, however, the achievement of optimum results requires that development and operating

programmes should be based on a knowledge of the reservoir characteristics, not merely in its initial state of equilibrium but also under the continually changing conditions brought about by the removal of oil and gas.

Unfortunately there are great difficulties involved in either a theoretical or an experimental approach to this study, and it is only in comparatively recent years that significant progress has been made and the science of 'reservoir engineering' has come of age.

The beginnings of the modern petroleum industry are commonly dated from the Drake discovery of 1859, and about the same time Darcy was publishing his classic researches on the flow of water through porous media. However, Darcy's results could not be adapted to the flow of oil in any precise sense until methods were devised for measuring pressure at depth, and also for measuring the relevant properties of oil under formation conditions of temperature and pressure. Work on these lines commenced shortly after the First World War in a few fields, but was mostly aimed at specific local problems, and was not widely publicized until the later 1920s. It was not until 1933 that Darcy's original concepts were properly modified and well enough established in the oil industry to permit of the definition of a basic unit of permeability. Even then the additional problems arising in the simultaneous flow of two or three fluids remained to be solved.

Experimental and theoretical work on these lines continued over the next several years and resulted in a radical revision of older ideas as to reservoir behaviour. However, the differential equations involved are mostly non-linear and as late as 1949 Muskat, in his standard textbook, had to remark that virtually all specific analytical and numerical considerations dealt with were restricted to idealized systems which have never been observed in practice.

During the last thirty years there have, of course, been many refinements in theory, and new experimental methods and techniques have become available. In particular, modern computers permit of solving more complicated equations, or equations with more complicated boundary conditions. However, the accuracy of any such calculations is ultimately dependent on the basic data supplied. The only direct information as to reservoir conditions is that obtainable at and in the very near neighbourhood of wells which are only a few inches in radius and often spaced a quarter of a mile or more apart. Elsewhere, conditions can only be inferred either by geological reasoning as to the probable continuity of lithological characteristics, or from observations on the producing behaviour of wells. As Muskat also indicated, any experiments carried out on an actual producing reservoir bring about irreversible and, in detail, unpredictable changes in fluid distribution. Particularly in the case of fields of complex lithology it may still not be possible to get sufficiently detailed knowledge early enough to make full use of the potentialities of modern reservoir engineering theory. At least in the early life of a new field, the development policy must be based in part on probabilities rather than on observed and proved facts.

In spite of these continuing difficulties, the practical value of a more scientific approach to production problems has come to be universally recognized, and has resulted in radical changes in operating policy and methods. At the same time, there have, of course, been major improvements in mechanical equipment, instrumentation, and the like.

In the space available it would be quite impossible to deal adequately with all

the varied aspects of production practice, and accordingly attention will be mostly confined to the basic principles peculiar to the development and operation of oilfields, with less space devoted to the mechanical details of equipment, and so on which will be dealt with in the following chapter. Even with this limitation it is not possible to deal with more than a small fraction of the exceptions to and deviations from general principles and methods.

Substantially more detailed and precise statements will be found in the texts listed at the end of the chapter, which also contain extensive bibliographies of the original literature.

The first section below deals with the relevant properties of the average reservoir and its contained fluids. This is followed by an outline of the methods available for estimating the reserves of newly discovered fields, which in turn involves a discussion of various types of reservoir behaviour.

Subsequent sections deal with the more important factors affecting the planning and control of reservoirs of various types, including a brief discussion of enhanced oil recovery methods.

PROPERTIES OF THE RESERVOIR AND OF THE FORMATION FLUIDS

The chemical composition of the crude oil and natural gas of commerce is described in a later chapter. Essentially they are both complex mixtures of hydrocarbons which may differ considerably from one reservoir to another. Even within a single accumulation the composition varies somewhat with depth in the oil column, and the distribution of the lighter components between the gas and liquid phases also varies with the temperature and pressure.

In an elementary discussion it is usual to talk of 'stock-tank' oil and gas as if they were entirely independent substances of invariable composition, the one dissolving in the other. Although not strictly correct, errors arising from this approach are effectively eliminated for many purposes by the use of experimentally determined values for the bulk physical properties of gas and liquid phases in contact under specified conditions.

The pressure in a virgin reservoir is usually at least as great as that which would be exerted by a column of water from surface and sometimes considerably greater. At a depth of 5000 ft, for example, pressures in the range 2000 to 4000 psi are common. Temperatures also increase with depth at rates up to about 2°F/100 ft.

The most general type of oil reservoir contains the three fluids, gas, oil, and water. Free gas is not always present, but there is always some dissolved in the oil, and in consequence the physical properties of the liquid hydrocarbon phase underground generally differ considerably from those of stock-tank oil. As the pressure is reduced by production below the 'bubble point' or saturation pressure, gas is progressively evolved from solution, the liquid phase shrinks in volume, and its density and viscosity increase. As the oil is brought to the surface, further changes occur in the same direction owing to removal of the last of the dissolved gas and a drop in temperature. These effects are determined experimentally, either by taking a sample from the bottom of a well which has been produced at a very low rate, or by recombining gas and oil separated at

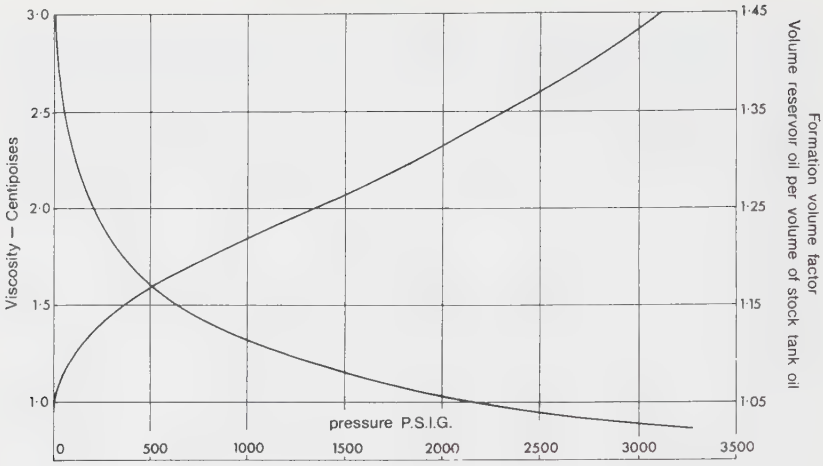

FIG. 1. Curves illustrating the effects of dissolved gas on the properties of a crude oil.

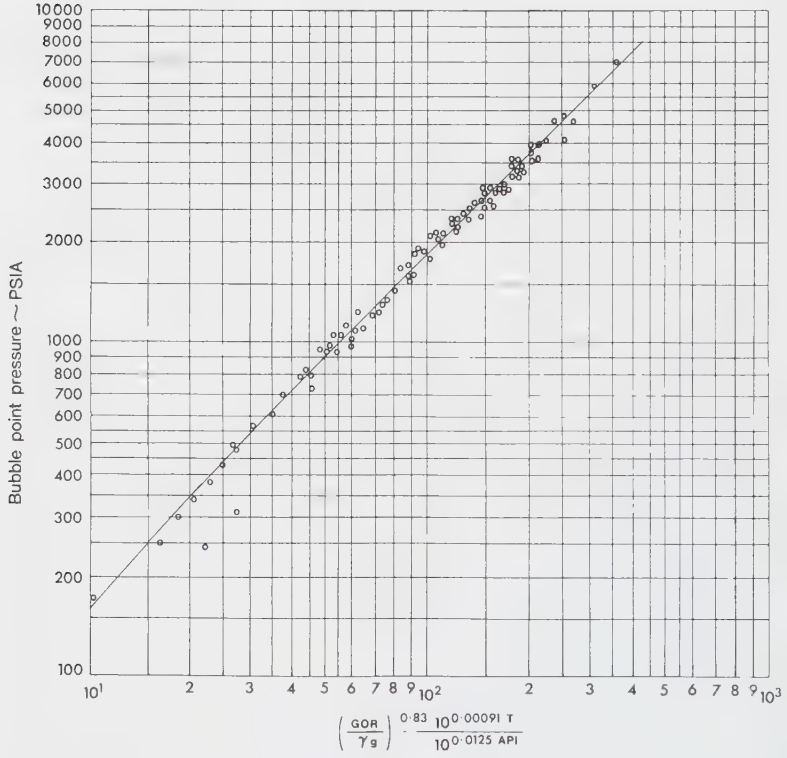

FIG. 2. Standing's correlation of bubble point pressure with dissolved gas/oil ratio, gas gravity, tank-oil gravity and temperature.

surface in the proportions in which they are produced and increasing the pressure and temperature to formation conditions.

Typical illustrative curves are given in Fig. 1, but there are of course considerable differences between one reservoir and another. For the greatest accuracy, curves of this type should be measured experimentally for each new reservoir, but reasonable estimates can often be obtained from empirical charts based on the gravities of stock-tank oil and gas.

Thus, for example, Standing developed an empirical correlation between the bubble point or saturation pressure in psia and the function

$$18\left[\left(\frac{R}{\gamma}\right)^{0.83} \frac{10^{0.00091T}}{10^{0.0125\rho}}\right]$$

where R is the dissolved gas/oil ratio in cu ft/brl, T the temperature in °F, γ the gas gravity, and ρ the oil gravity in °API. For the crudes tested, this function is equal to p at pressures above 1000 psia, and falls somewhat more rapidly than p at lower pressures (Fig. 2).

The typical oil-bearing formation is microporous rather than cavernous. It may resemble ordinary beach sand, but the individual grains are often bonded into a rigid mass which is occasionally traversed by open fissures. The structure may be fairly uniform over a considerable area, but frequently exhibits marked variations which considerably complicate the production problem. For the moment these variations will be left out of account, and the oil considered to be contained entirely within the microscopic pores of a rock with reasonably uniform characteristics.

In the course of geological time the three reservoir fluids tend to separate according to their densities, with water below and free gas above the oil. However, almost invariably the rock is preferentially wetted by water, and owing to the effect of interfacial forces the separation is not complete. In the basal part of the reservoir the pores are completely filled with water. At higher levels some of the water is replaced by oil, the percentage of oil increasing with the height while the water is progressively confined to the smaller pores.

Within this transition zone, each of the two phases is continuous and there is a capillary pressure across the curved interfaces which increases with height, and is balanced by the difference in liquid densities. Both oil and water can move under the influence of a pressure differential; it is in fact not possible to produce water-free oil from this part of the reservoir. However, at a sufficient height above the base the water content drops to what, in practice, may be regarded as an irreducible minimum, the continuity of this phase is broken, and the water is no longer mobile.

A somewhat similar condition occurs at the upper contact between oil and gas, but commonly there is an intermediate zone in which oil is initially the only mobile fluid. In what follows, attention will be concentrated on this last section, and the complications arising from the transition zones mostly ignored.

With this picture in mind there are evidently two important bulk characteristics of the formation—its capacity for containing oil and the resistance to flow. Both are determined by the microscopic structure of the rock, which also controls the distribution of the various fluids in the initial transition zones and under the changing conditions which develop in the course of production.

The porosity of a rock may be defined as 1 minus the fraction of the bulk volume comprised of solid matter. In practice we are concerned with the effective porosity, that is to say with the fractional volume of connected pores, but this rarely differs appreciably from the total porosity. There is evidently no difficulty in principle in measuring this quantity and several practical methods are available, given a suitable sample of the formation rock.

With any of these methods, abnormal difficulties may arise on occasion. For example, if a core is cut in a completely uncemented sand it will tend to expand as the pressure is released on bringing it to the surface, and to disintegrate completely on extraction and drying. In such cases, or where no actual samples of the formation are available, estimates of porosity may be made from one or more of the logging devices described in Chapter 3—electric, acoustic, density, and neutron. None of these alone will give a strictly unequivocal value for the porosity. For example, the readings of a density log are dependent both on the porosity and on the densities of the rock matrix and of the contained fluid. Again, the various micro devices measure the electrical resistivity of the formation saturated (or nearly so) with mud filtrate of known characteristics. This resistivity is a function not only of the porosity but also of the pore structure—the 'tortuosity' of the path taken by the electric current. Consequently, if only one type of log is available, it is necessary to make assumptions as to the lithological character of the formation, but these assumptions can be checked by cross plotting if two or more types of log have been recorded.

Such measurements as these yield the total or effective porosity of the rock but, as already mentioned, there is always some water present which limits the volume of porosity available for containing oil. Even in formations capable of producing dry oil, the amount may vary from about 10 to 50 per cent or more of the pore space, depending on the pore structure.

It is evidently a simple enough matter to determine the amount of water contained in a core sample, but such measurements are generally not indicative of underground conditions, having regard to the effects of flushing by water in the drilling mud and the release of pressure. It is therefore necessary to resort to indirect methods which are broadly speaking of three kinds.

First, if an oil-base mud is used in drilling it will not displace water from a core to a point below the 'irreducible' minimum, and direct measurements of water saturation should give satisfactory results. Secondly, estimates may be made from the results of electric logging described in an earlier chapter. Space is not available to discuss all the various complications, but in brief outline the method consists in comparing the measured resistivities obtained by a micro device on the one hand, and a deep penetration device on the other. The former measurement gives the resistivity (R_{xo}) of a zone which has been thoroughly flushed by mud filtrate of a known resistivity (R_{mf}) to a certain residual saturation with this filtrate (S_{xo}). The deep penetration device (suitably corrected) yields the true resistivity (R_t) of the formation in its natural condition with a certain saturation (S_w) of formation water whose resistivity is R_w which can be determined either from samples or from the spontaneous potential curve.

If the formation is fully saturated with water, we have

$$\frac{R_{xo}}{R_{mf}} = \frac{R_t}{R_w} = F \text{ (the formation factor)}$$

Otherwise there is the empirical relationship

$$F = S_{xo}^2 \frac{R_{xo}}{R_{mf}} = S_w^2 \frac{R_t}{R_w}$$

Hence S_w can be determined if either F or S_{xo} is known or can be reasonably assumed on the basis of core experiments, or observations on a similar formation known to be 100 per cent water-saturated.

The remaining method for estimating the interstitial water content of a formation is dependent on the laboratory determination of a capillary-pressure curve. If a core saturated with water is placed in contact with a rigid plate of low permeability (with very fine pores), and a steady gas pressure is applied to the surface of the sample, water will be expelled until the applied pressure is balanced by the surface tension across the curved interface. By varying the pressure, curves similar to those in Fig. 3 may be obtained. For comparison with actual formation conditions it is necessary to correct for the differences between the interfacial tension of oil and water on the one hand, and gas and water on the other, and to observe that in the formation the balancing pressure is derived from the difference in density between oil and water. Hence it is possible to calculate the interstitial water content at any given height above the free-water level. Variants of this general method include the centrifuging of water-saturated cores on the one hand, and, on the other, forcing mercury into a dry core at progressively increasing pressures.

Turning now to the other important bulk characteristics of the formation, namely, its resistance to flow, this is considered in terms of its reciprocal, the permeability. Darcy's law was originally established for the flow of water under

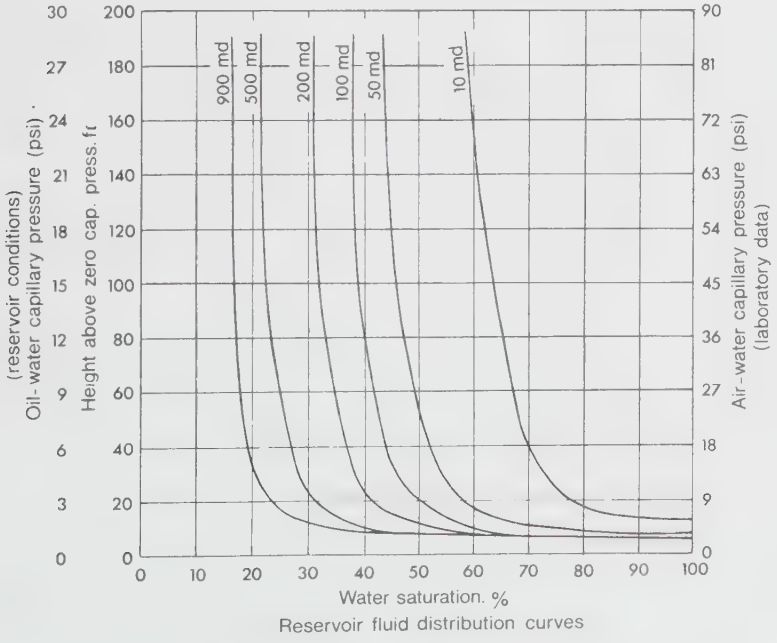

Fig. 3. Typical capillary pressure curves (after Wright and Wooddy).

its own head through a porous sand, but has since been generalized and demonstrated experimentally for any homogeneous fluid moving under the influence of an applied pressure gradient. For steady linear flow the appropriate equation is

$$Q = \frac{Ak}{\mu} \frac{dP}{dL}$$

where Q = volume rate of flow (cc/sec) (in the case of gas flow the volume is measured at the mean pressure); A = cross-sectional area of rock (sq. cm); μ = viscosity of fluid (centipoises); dP/dL = pressure gradient at right angles to the cross-section (atm/cm); k = a constant characteristic of the porous medium, and called the permeability; with the units indicated in brackets above k is expressed in the common practical unit, the darcy.

The formula is analogous to that for flow through capillary tubes and, like it, begins to break down if the rate of flow exceeds some critical value. In practice this value is rarely approached in the movement of oil and water, but is quite commonly exceeded near a well which is producing gas.

Given samples of the formation, the experimental determination of permeability is evidently simple enough in principle. It merely involves measuring the rate of flow of a suitable fluid under a measured pressure gradient. For routine purposes it is common to use gas flowing through a dry core, and to record the volumetric rate at the mean pressure of the system, which is strictly appropriate for a perfect gas. However, various complications have to be allowed for in practice. Working at low pressure with a sample whose pore diameters are of the same order of magnitude as the mean free path of the gas molecules, slippage occurs and the calculated permeability will be too high. Again many sands contain clay particles which shrink on drying, and significantly different permeability values may be obtained depending on whether gas, fresh water, or brine is used in the determination. Most sands are in some degree anisotropic and offer less resistance to flow in the direction of bedding than at right angles to it, and some reservoir rocks have large and erratically distributed openings or fissures, so that laboratory samples of reasonable size may not always be representative.

If no actual samples are available there is no really reliable method of determining permeabilities from the various well-logging devices, although under favourable conditions estimates can be made from empirical formulae relating porosity, permeability, and water saturation.

The porosity of reservoir rocks of commercial interest usually falls in the range of 10 to 40 per cent, and the permeability may vary from less than 1 millidarcy to several darcys. However, the two properties are not directly related; for example, two geometrically similar sands will have the same porosity but permeabilities which are proportional to the square of the scale factor. Hence, a reservoir may have a reasonable porosity but be non-commercial because the permeability is too low to permit of reasonable producing rates.

In any case, the permeability as so far defined is adequate only for the calculation of limited types of flow problems. Within the oil–water transition zone, for example, oil and water can move together through the same pores. Even where the interstitial water is effectively immobile, the evolution of gas

from solution in oil leads to the introduction of a second mobile phase into pores originally containing one only. Under such conditions, it has been found experimentally that Darcy's law can still be considered to hold, except that the permeability is a function not only of the pore structure but also of the percentage saturations with the various fluids. Thus, the resistance to the flow of oil increases sharply as the gas content of the pores increases; for constant saturation the flow can be calculated using an appropriate fraction of the normal permeability, but when the saturation varies with time the permeability in Darcy's equation is no longer a constant.

There is only a small range of saturations within which all three fluids have appreciable mobility, and for most purposes it is sufficient to consider two-phase flow. Typical curves illustrating the effect of saturation on relative permeability are given in Fig. 4. The exact shape of the curves varies with the nature of the porous medium, and no single set of curves is universally applicable.

This is illustrated by the following tabulation of an empirical method of estimating two-phase (oil, gas) permeabilities taken from published literature. If the single-phase permeability of a rock is k and the two-phase permeabilities to oil and gas, respectively, are k_o and k_g, then $k_{ro} = k_o/k$ and $k_{rg} = k_g/k$ are

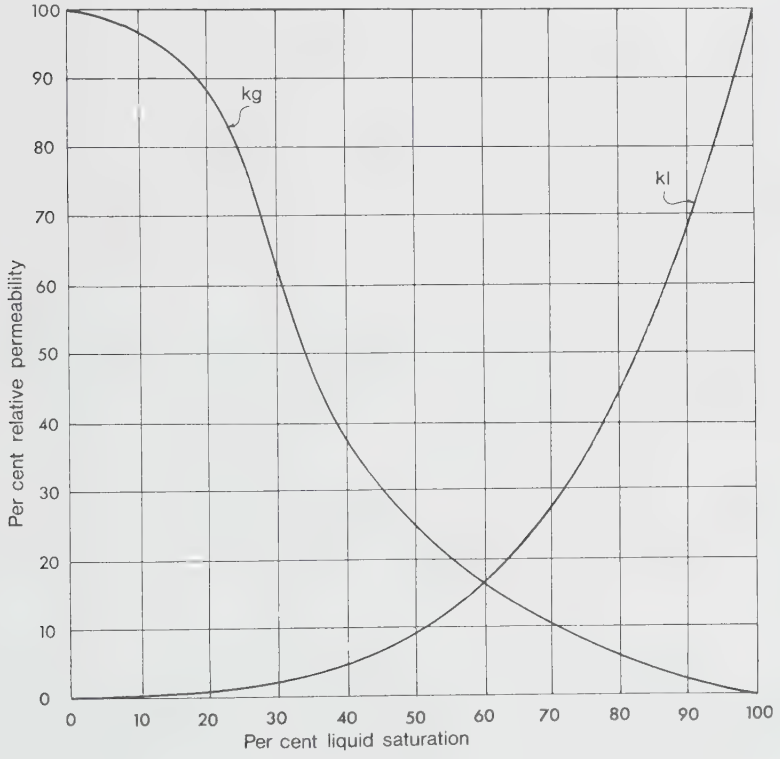

FIG. 4. Typical permeability/saturation data for unconsolidated sands. k_l and k_g refer to liquid and gas phases. (After Wyckoff and Botset.)

defined as the relative permeabilities. Taking S as the fractional oil saturation divided by (1 − the irreducible water saturation) approximate values of k_{ro} and k_{rg} are indicated in Table I.

The experimental measurement of relative permeability obviously involves more complicated techniques than those needed for determination of homogeneous fluid permeability. Difficulties in deriving unequivocal values arise from the heterogeneity and anisotropy of many core samples, and also from the fact that both capillary pressure and relative permeability curves are dependent to some extent on the previous history of the sample. In particular, there are significant differences if a given saturation is approached by water replacing oil or vice versa.

TABLE I
Relative Permeabilities, Gas and Oil, for Various Formations

Types of formation	k_{ro}	k_{rg}
Unconsolidated sand, well sorted	S^3	$(1-S)^3$
Unconsolidated sand, poorly sorted	$S^{3.5}$	$(1-S)^2(1-S^{1.5})$
Cemented sandstone, oolitic limestone, etc.	S^4	$(1-S)^2(1-S^2)$

Whatever methods are used for arriving at the values of these parameters, it has to be remembered that the results strictly apply only to the core samples actually used (which incidentally no longer form a part of the producing reservoir) or, in the case of log determinations, to a short distance around a well. Normally porosity, permeability, and water saturation vary both vertically and laterally through the reservoir and the range of variation may be great. For example, reported figures for the Woodbine sand of East Texas give the range of formation thickness from 2 to 45 ft, of permeability from 0.1 to 13 840 millidarcys, of porosity from 9.7 to 38.2 per cent and of interstitial water saturation from 14 to 65 per cent.

In making any practical use of such figures, it is necessary to consider whether the reservoir can be divided into a number of reasonably uniform blocks each with appropriate values of the various parameters which are relevant to any particular problem under consideration. This is by no means always an easy matter, particularly in the early stages of development when the amount of information is necessarily limited. At a later stage, when some production experience has been gained, various methods are available for cross checking some of the earlier estimates and assumptions; reference to some of these methods is made later in the chapter.

RESERVE ESTIMATES

When a new reservoir is discovered it is obviously important to determine how much oil and/or gas it contains, for on this figure will depend the justification for undertaking the expense of development and production and the design of these operations.

Natural oil accumulations may contain as little as a few thousand barrels or

less of recoverable oil or as much as several thousands of millions of barrels. For example, it has been reported from the United States in recent years that one exploratory well in ten or so has found some oil and gas, but only one in forty has found as much as one million barrels of oil, or an equivalent amount of gas, which is taken as a rough measure of the smallest accumulation which can be profitably produced. On the other hand the East Texas field, discovered in 1931, has already produced close to 5×10^9 brl, and there are several still larger single accumulations, notably in the Middle East. Naturally, the minimum size of a reserve which is worth developing is dependent on a variety of factors, such as proximity to a pipe line and market, drilling costs, and so on. A field of a size that could not possibly pay out if found in Northern Alaska might be highly profitable if it were located in Texas. In any event, an estimate of the amount of oil available is of primary importance.

In the period immediately following a discovery, and in the early days of development, only the volumetric method is available. The first step is to define the limits of the oil-bearing section and hence obtain the total volume (usually expressed in acre-feet). This is a problem for the geologist, with perhaps some geophysical help, and will not be discussed in detail here. It may be observed, however, that in many areas a large total amount of oil is distributed among a number of small and independent reservoirs, and it becomes a matter of some difficulty to define the limits of each without an excessively large number of wells, many of then either complete failures or poorly located for production. As much geological skill may be needed for efficient development as is required in the preliminary exploration.

It is next necessary to determine the average porosity of the reservoir rock and also the percentage of the pore space occupied by water as already discussed. From these figures one can obviously calculate the amount of reservoir oil in place, and a measurement of the shrinkage of a sample of oil on reduction to atmospheric pressure and temperature permits of converting this value to stock-tank oil.

There is evidently considerable scope for error in a calculation of this type based on limited evidence. The geological and geophysical evidence may be quite inadequate, and the formation characteristics determined from the cores or logs of a single well may be unrepresentative of the overall reservoir average. It is therefore advisable and customary to make early estimates on a conservative basis to be refined later as additional information becomes available.

After a field has actually been produced for some time, it may be possible to check the estimate of oil in place by means of a 'material balance' calculation. If one considers a closed tank containing known amounts of oil, gas, and water of specific physical properties, it should clearly be possible to calculate the decline in pressure arising from removing known amounts of the various fluids. Conversely, if the change in pressure is measured after various increments of production, the original amounts of oil, gas, and water in place can be calculated. The method is, however, very sensitive to errors in the average pressure which may arise in various ways. If, for example, there is a thick oil column in a highly permeable formation, gas evolved from solution can migrate upwards, with a resulting uncertainty in the average pressure to which the residual gas is subjected. Again, since the formation fluids are compressible, the

pressure at a point in the reservoir does not instantaneously adjust to changes in producing rates. In particular, a relatively small oil and gas accumulation may be in contact with a very large aquifer or water-bearing section, and it would be quite impracticable to shut in production for long enough for true pressure equilibrium to be reached throughout. In this case, if the material balance method is used with the assumption that there is no significant amount of water associated with the oil reservoir, repeated calculations at later times will result in progressively increasing estimates of oil and gas in place. It is then necessary to assume suitable rates of water encroachment which will yield substantially constant values for oil and gas in place, and which at the same time are compatible with the basic theory of unsteady flow of a compressible liquid against a varying pressure. There are several detailed variants of this approach depending on how much information is available, or can be assumed as to the properties of the aquifer.

In practical applications the results of a material balance calculation must be regarded as subject to a wide range of probable error. For example, in the case of the Jones sand at Schuler the oil in place was calculated at some thirty times within a three-year period and average values of either 102 MM brl with a rms deviation of 1.85 per cent, or 75 MM brl with a deviation of 1.64 per cent could be obtained, depending on assumptions as to the gas-cap volume on the one hand and water encroachment on the other. The method, in fact, needs to be used with some discretion, and rather as a supplementary tool than as an absolute standard.

In any event, the oil in place is only one of the factors which need to be determined in the course of reserve estimating. It is also necessary to estimate how much of it can be recovered. The practical percentage recovery varies over a very wide range, and the factors affecting it will be discussed in later sections, with brief notes as to methods of calculation to be applied to individual reservoirs. For the moment it may be observed that after a reservoir has been fully developed and on production for some time, it may be possible to get an estimate of the remaining producible reserves by extrapolating a suitable curve of past performance down to the economic limit. Examples of plots which often yield curves of simple form are producing rate versus time: cumulative production versus pressure: and cumulative production versus water/oil ratio. Here again the method of decline curve analysis needs to be used with discretion, since, for example, the relative effects of various natural forces may vary with time, and at any particular time the rate of production can be varied by extraneous controls which distort the 'natural' decline. On broad lines the influence of such factors will be indicated in later sections: for the moment some general remarks on the significance of reserve estimates may be of interest.

First, it is necessary to distinguish between the primary reserves, recoverable by simply making use of natural forces, and secondary reserves which represent the additional recovery obtainable by some method of artificial stimulation. Nowadays it is common practice to apply secondary methods at a relatively early stage and well before all primary recovery has been obtained. Nevertheless, it is necessary to estimate what the primary recovery would have been in order to consider the economic justification of the secondary methods. (The classical method of secondary recovery involved the injection of gas or water. In recent years increasing attention has been paid to modified or alternative

TABLE II
Classification of Petroleum Reserves

Energy source	Degree of proof	Development status	Producing status
Primary Reserves Those reserves recoverable commercially at current prices and costs by conventional methods and equipment as a result of natural energy inherent in the reservoir	*Proved* Primary reserves which have been proved to a high degree of probability by production from the reservoir at a commercial rate of flow or in certain cases by successful testing in conjunction with favourable complete core-analysis data or reliable quantitative interpretation of log data *Probable* Primary reserves which have not been proved by production at a commercial rate of flow, but—being based on limited evidence of commercially producible oil or gas within the geological limits of a reservoir above a known or inferred water table—are susceptible to being proved by additional drilling and testing *Possible* Primary reserves which may exist but where available data will not support a higher classification	*Developed* Proved reserves recoverable through existing wells *Undeveloped* Proved reserves from undeveloped spacing units in a given reservoir which are so close and so related to the developed units that there is every reasonable probability that they will produce when drilled.	*Producing* Developed reserves to be produced by existing wells from completion interval(s) open to production *Non-producing* Developed reserves, behind the casing or in certain cases at minor depths below the producing zones, which will be produced by existing wells
Secondary Reserves Those reserves, recoverable commercially at current prices and costs, in addition to the primary reserves as a result of supplementing by artificial means the natural energy inherent in the reservoir, sometimes accompanied by a significant change in the physical characteristics of reservoir fluids	*Proved* Secondary reserves which have been proved to a high degree of probability by a successful pilot operation or by satisfactory performance of full-scale secondary operations in the same reservoir or in certain cases a similar nearby reservoir producing from the same formation *Probable* Secondary reserves which are thought to exist in a reservoir by virtue of past production performance or core, log, or reservoir data, but where the reservoir itself has not been subjected to successful secondary operations *Possible* Secondary reserves from reservoirs which appear to be suited for secondary operations but where available data will not support a higher classification	*Developed* Proved reserves recoverable through existing wells from a reservoir where successful secondary operations are in progress *Undeveloped* Proved reserves which will be produced upon the installation and operation of a secondary recovery project and/or by the drilling of additional wells	*Producing* Developed reserves to be produced by existing wells in that portion of a reservoir subjected to full-scale secondary operation *Non-producing* Developed reserves to be produced by existing wells upon enlargement of the existing secondary operations

methods—sometimes called 'tertiary' recovery but more suitably 'enhanced oil recovery'—EOR.)

Reserve estimates are commonly also classified under such headings as proven, probable, and possible. One such classification (by Arps) is given in Table II, but various authorities have used somewhat differing definitions, and in any case there is scope for more or less conservatism in assessing the degree of proof in respect of each class of reserves. Quoted reserve figures are therefore not always comparable, and in particular, early estimates of proven reserves commonly need progressive modification as the developed area expands and successful secondary recovery methods are introduced.

Table III compares the estimates made by US Government agencies on various groups of fields at two dates separated by fifteen years.

The large difference in respect of the latest discoveries dealt with no doubt reflects in large part the transfer of reserves from the probable to the proven category, and a similar large difference in respect of much earlier discoveries is the result of the later introduction of secondary methods.

TABLE III

Estimates of Oil Reserves, Million Cubic Metres

Fields discovered during period	PAW estimate 1945	NPC estimate 1960	% changes
1919	2 324	2 757	+19
1920–24	840	1 417	+69
1925–29	1 145	1 582	+38
1930–34	1 684	2 121	+26
1935–39	1 449	2 307	+59
1940–44	832	1 500	+80
1920–44	5 950	8 927	+50

PAW—Petroleum Administration for War.
NPC—National Petroleum Council.

One further point may be worth noting. A well or field will be abandoned when the cost of producing additional oil exceeds the value of it, even though it is still technically possible to extract more oil. Consequently the economic reserves will always be somewhat less than the technically possible.

In dealing with large and highly profitable fields or global estimates, this may be of no great practical significance from the point of view of policy or the planning of operations. However, the economic life of a small reservoir in an area where overheads are high will be dependent on whether or not other discoveries are made in the same region to share the overheads. Further, the time of abandonment may be, say, twenty years ahead, and calculation of the economic limit on the basis of current costs and prices involves the tacit assumption that these values will in the rather distant future always vary in step, which is by no means necessarily the case. It is true, of course, that near the time of abandonment the profit per barrel will in any case be small, and errors in the economic assumptions of the type indicated above may have little significant effect on the estimated present worth of a particular reserve.

In this section, however, we are primarily concerned with estimates of recoverable oil, and it should be apparent that any such estimate needs to be assessed in the light of its precise definition and underlying assumptions of various kinds.

RESERVOIR BEHAVIOUR

In the previous section, reference was made to the fact that it is not practicable to recover all the oil in a reservoir. Here the limiting factors will be discussed, together with methods of completing reserve estimates by estimating the percentage recovery.

Oil reservoirs differ very greatly from one another in shape and size, in formation characteristics and in oil properties, and all of these variations affect performance in detail: in addition, there are important differences in the way in which oil is expelled. On completion of a well the pressure at its foot is reduced, and flow commences as a result of the differential pressure thus established between the well and more remote parts of the reservoir. Unless the fluid so removed is replaced, the average formation pressure necessarily drops at a rate dependent on the rate of production, and on the average compressibility of the remaining fluids. If there is an initial free gas cap, it expands with falling pressure and gas replaces oil produced from wells lower on the structure: similarly, gas is evolved from solution in oil when the pressure drops below the saturation point, and the gas accumulates within the oil zone. Water also is slightly compressible, and if the amount of water in contact with an oil reservoir is large enough, a considerable quantity of oil can be displaced by expansion of water as the pressure falls.

In any particular case, one or other of these factors may be the most important and reservoirs can be roughly classified according to whether a gas cap, dissolved gas, or water encroachment can be regarded as the principal agent in expelling oil. However, it is usually necessary to consider the resultant effect of two or more of these factors, the relative importance varying both with time and the rate of production. Frequently also it is desirable to alter the natural balance of forces by artificially injecting either gas or water. The behaviour of a reservoir (that is to say, the rate of decline in pressure and producing rate) is determined by the way in which these various forces are controlled.

From what has been said earlier, it will be clear that any attempt at precise and detailed calculation of the course of events would entail an unattainable amount of knowledge as to reservoir characteristics. It is evident, also, that the simple formulation of Darcy's law needs elaboration to deal with actual oilfield problems. Not only are we dealing with three fluids which are compressible, but flow is not generally linear; it is rather convergent towards producing wells and divergent at injection wells. Pressure gradients are therefore not everywhere uniform, and stable flowing conditions are not reached instantaneously as rates of offtake are varied.

The simplest case is evidently that of a pure gas (single phase) reservoir at moderate temperature and pressure. In principle it should be possible to recover all the gas in place by sufficiently dropping the pressure, but there are some complications. If the pressure is effectively maintained by encroachment

of water from an extensive aquifer, some gas will be trapped by capillarity behind the advancing water front, so that no more than perhaps 80 per cent of the gas will be recovered in practice. On the other hand, if the pressure declines there will be an economic limit when the cost of compression becomes excessive, so that in estimating reserves it is necessary to forecast future production.

As already indicated, rates of flow are often too high for Darcy's law to hold, and it is customary to test a new well at varying rates of flow and to plot $P_s^2 - P_f^2$ (P_s = closed-in pressure, P_f = flowing pressure) against the rate on a log–log scale. This is equivalent to plotting the product of the pressure differential and the mean pressure and for Darcy's law should yield a straight line of unit slope. Commonly the equation $Q = C(P_s^2 - P_f^2)^n$ (with Q the rate of flow, C and n constants) applies and $n < 1$ is characteristic of the formation in question. However, various precautions need to be taken, both in measuring and in using these results. Obviously in predicting future performance, allowance has to be made for variations in the Boyle's law deviation factor as the reservoir pressure declines. At the same time, if the initial tests are of short duration, steady flowing conditions may not be reached throughout the entire reservoir, and the results of one test may be distorted by the residual pressure variations due to a previous test. There is insufficient space available here to discuss these matters in detail, but a comprehensive review of the various methods will be found in Reference 3.

Of perhaps more general interest is the case of the typical oil reservoir. The appropriate differential equations of flow have been formulated by Muskat as follows:

$$\nabla \cdot \left[\frac{S_o k_o}{\beta_o \mu_o} \nabla(p - \gamma_o g z) + \frac{S_w k_w}{\beta_w \mu_w} \nabla(p - \gamma_w g z) + \frac{\gamma_g k_g}{\mu_g} \nabla(p - \beta_g g z) \right] = f \frac{\partial}{\partial t} \left(\frac{S_o \rho_o}{\beta_o} + \frac{S_w \rho_w}{\beta_w} + \gamma_g \rho_g \right)$$

$$\nabla \cdot \left[\frac{k_o}{\beta_o \mu_o} \nabla(p - \gamma_o g z) \right] = f \frac{\partial}{\partial t} \left(\frac{\rho_o}{\beta_o} \right)$$

$$\nabla \cdot \left[\frac{k_w}{\beta_w \mu_w} \nabla(p - \gamma_w g z) \right] = f \frac{\partial}{\partial t} \left(\frac{\rho_w}{\beta_w} \right)$$

$$\rho_o + \rho_w + \rho_g = 1$$

where the subscripts o, g, w refer to the oil, gas and water phases: S is the volume (at standard conditions) of gas in solution per unit volume of liquid phase at standard conditions; k is the permeability, β the formation volume of the liquid phase, μ the viscosity, γ the phase density, p the pressure, f the porosity, t the time, and ρ the phase saturation as a fraction of the porosity.

s, p, μ, and γ are empirical functions of the pressure and the ks are empirical functions of the saturations.

Even this sufficiently complex formulation is not complete. It does not allow for capillary pressure gradients, for anisotropy or indeed for variations in formation characteristics within an extensive reservoir, and it also implies that phase equilibrium exists everywhere and at all times.

A precise analytical solution of these equations is not possible, and it is necessary to resort to some method of approximation, and usually also to make simplifying assumptions. For example, in the simplest case of the steady flow of a single fluid through a uniform reservoir, the base equation reduces to the Laplace equation, and for unsteady flow of a single fluid of constant compressibility, it reduces to the diffusivity equation. Both of these can be solved analytically for reasonably simple boundary conditions, and otherwise electrical analogues can be constructed using a network of either simple resistivities in the first case, or of resistivities plus capacities in the second.

Such analogue computers have been extensively used in the past, but in their simplest form they do represent highly idealized systems. If allowance is to be made for changes in compressibility arising from the evolution of gas, the electrical capacities in the model must be variable, and similarly the resistance network must be both variable and more complicated to allow for changes in permeability and composition of the moving fluid. In recent years the introduction of progressively more powerful digital computers has led to the widespread use of such instruments in reservoir modelling. The reservoir and its associated aquifer are notionally divided into a large number of blocks with appropriate values of the relevant parameters assigned to each, and with offtake or input wells located in some of them. Flow through the model resulting from assumed applied pressure variations in the latter blocks can then be computed from the normal equations of multi-fluid flow across the block boundaries and the material balance equation applied within each block, and hence the future performance of the reservoir can be forecast.

It is not of course to be expected that early estimates of this kind will in the event prove to be very accurate. Continued development drilling and production are likely to provide new evidence, perhaps of minor faulting or localized zones of abnormal permeability, for example. The model will then need progressive modification in detail to match the past producing history.

Clearly programming for the computation of reservoir performance based on such a model will be very complex and cannot be treated in the limited space here available. A detailed discussion will be found in References 8 and 9.

For illustrative purposes, much more elementary methods may be used, some of which are briefly outlined later. Not uncommonly an estimate of sufficient accuracy for the purpose of preliminary planning can be obtained from generalized curves and tabulations of the type shown in Figs 5 and 6 and Table IV, coupled with the assumption of a simple exponential type of production decline curve.

To begin with, we may take the ideal case of a uniformly porous sand containing only oil with its dissolved gas. As the pressure is reduced, small amounts of gas evolved from solution accumulate in the pores, and increase the resistance to flow of oil without the gas itself being mobile, but, as the concentration increases, the gas bubbles eventually join up to form a continuous phase, and from then on both fluids move through the formation.

As illustrated in Fig. 4, the permeability of a porous formation to gas increases, and the permeability to oil decreases as the oil saturation decreases. Hence, with continued production, the produced gas/oil ratio tends to rise, this tendency being accentuated both by shrinkage of the liquid-phase volume and by the increase in its viscosity with loss of dissolved gas. On the other hand,

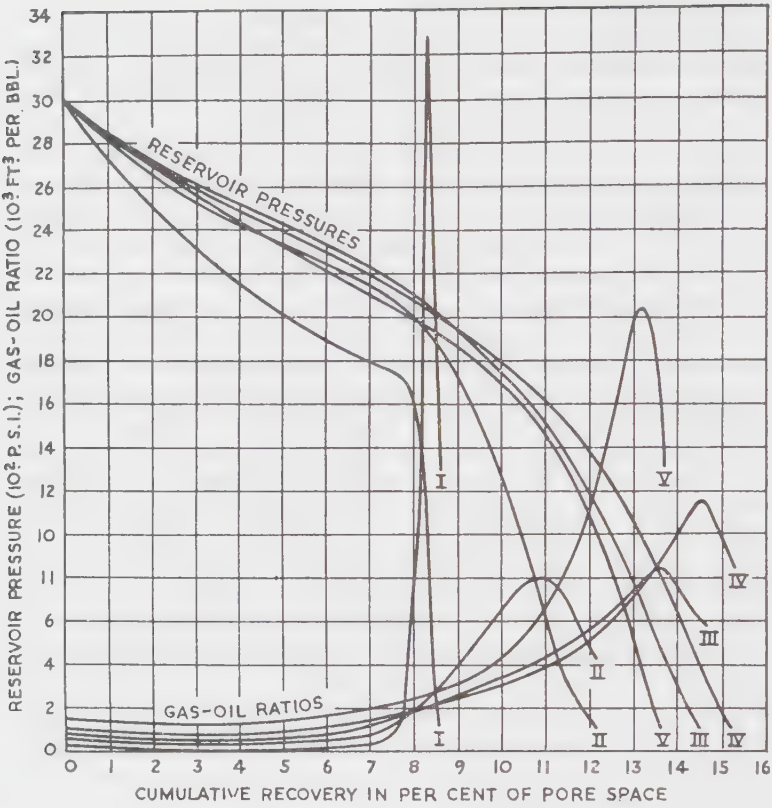

FIG. 5. Calculated pressure and gas–oil ratio histories of hypothetical solution gas drive reservoirs producing oils of different API gravity. Curves I-V refer to crude oils of 10, 20, 30, 40, and 50° API respectively. Connate water saturation assumed equal to 25 per cent in all cases. (After Muskat and Taylor, *Petroleum Engineer*, 1946).

since, in applying Darcy's law to gases, the volumetric rate of flow is calculated at the mean pressure, there is a factor tending to reduce the gas/oil ratio (corrected to standard conditions) as the mean formation pressure drops.

The production from a reservoir which originally contains only oil with dissolved gas, is therefore characterized by three gas/oil ratio trends. Initially, there is a short period of steady or slightly falling gas/oil ratio until continuous gas passages are established, then the gas/oil ratio rises fairly sharply until the pressure is nearly exhausted, and finally it declines to low values again. With this mechanism, production can theoretically continue until the pressure through the reservoir has been reduced to zero, with all of the gas but not all of the oil produced.

In principle, simplified methods commonly used for calculating this type of performance are based on the assumption of uniform production from every point in the reservoir (i.e. they implicitly neglect pressure gradients) and then using a stepwise calculation which combines the material balance principle on the one hand, and the relative permeability concept on the other. Thus, for

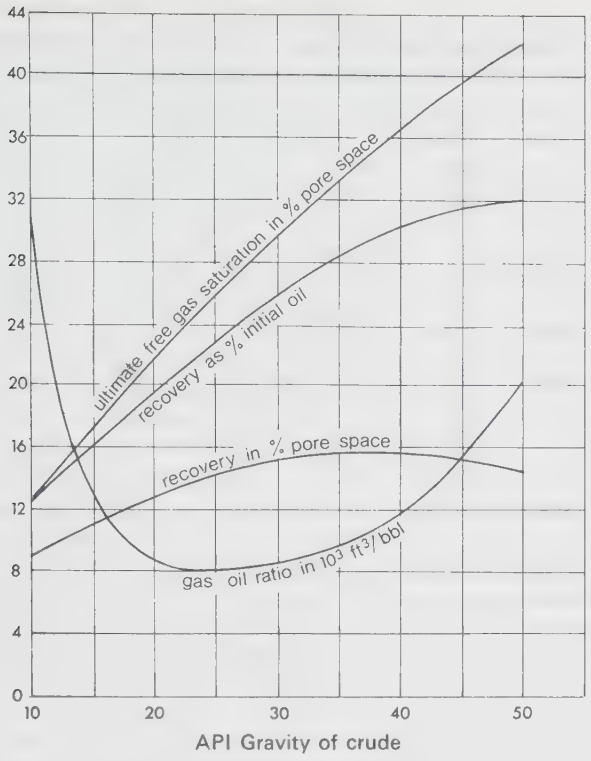

FIG. 6. Calculated ultimate recoveries, free gas saturations (at 100 psi) and maximum gas/oil ratios of hypothetical solution gas drive reservoirs as functions of the crude gravity. (After Muskat and Taylor.)

example, given an initial pressure and oil saturation, the instantaneous producing gas/oil ratio is determined by the k_g/k_o relationship, and assuming this constant for a small finite production of oil, the residual amounts of stock-tank oil and gas in a unit block are known. Assuming equilibrium conditions, these fluids will be distributed between gas and liquid phases at a calculable pressure, and these conditions can be used as the starting point of the next step in the calculation. Practical methods of computation commonly depart somewhat from this simplified description, the equations being set up to deal with fixed decrements of pressure of appreciable size, with some process of trial and error to allow for variations in the producing gas/oil ratio within each interval.

Leaving aside the question of the probable accuracy of such simplified methods as applied to any particular reservoir, they can be used to indicate, at least qualitatively, the effect of various factors on percentage recovery.

From general considerations a high initial pressure would be expected to favour high recovery of oil, and it does in fact do so, although the effect is smaller than might be thought. The higher the pressure the greater the amount of gas that can be held in solution in oil and hence, if the oil is fully saturated at the higher pressure, there is greater initial reserve of energy available. However, the

TABLE IV

Computed Recovery in Barrels per Acre-Foot per Per Cent Porosity by Dissolved Gas Drive

Initial pressure psi approx.	Oil gravity °API	Solution gas/oil ratio cu ft/brl	Sand or sandstone (water saturation 25 per cent)			Limestone, dolomite or chert (water saturation 15 per cent)	
			Unconsolidated	Consolidated	Highly cemented	Vugular	Fractured
750	15	60	7.2	4.9	1.4	2.6	0.4
450	30	60	12.0	8.5	4.9	6.3	1.8
250	50	60	19.2	13.9	9.5	11.8	5.1
2 000	15	200	7.0	4.6	1.8	2.6	0.5
1 350	30	200	11.6	7.9	4.4	5.8	1.5
700	50	200	19.4	13.7	9.2	11.4	4.4
5 250	15	600	7.6	4.8	2.5	3.3	0.9
3 400	30	600	10.5	6.5	3.6	4.7	1.2
1 750	50	600	15.0	9.7	5.8	7.2	2.1
5 100	30	1 000	12.3	7.6	4.5	5.4	1.6
2 750	50	1 000	12.0	7.2	4.1	5.8	1.2
5 000	50	2 000	10.6	6.4	4.0	4.3	1.5

efficiency with which this energy is used falls off rapidly as the depletion of the reservoir increases, and in the higher ranges of depletion, very high gas/oil ratios are necessary. At the same time the amount of stock-tank oil originally contained in a given formation is reduced by the liquid-phase volume of the dissolved gas, so that a large increase in pressure results in only a relatively small increase in the recovery from unit volume of formation.

Variations in the oil density have a somewhat similar effect. Broadly speaking the lower the density of oil the greater the amount of gas that it can dissolve at a given pressure, and also the lower its viscosity. The low viscosity tends to result in an increase percentage recovery, while increased shrinkage limits the advantage so obtained.

In Figs 5 and 6, some calculated curves illustrate the effect of these various factors on the performance of reservoirs with the same sand characteristics and initial pressures, but carrying oil of different densities; the viscosity and dissolved gas content of the oil are assumed to be related to the density according to averaged and fairly representative functions. It will be observed that although the recovery expressed as a percentage of the oil in place increases with the API gravity (Fig. 5), the actual amount of oil recovered increases up to a point, and then decreases (curve 5, Fig. 6).

One factor has, however, been left out of the discussion so far. It has been implicitly assumed that both the oil and the free gas in the formation are subject to the same pressure gradient, whereas in fact there is an additional gravitational force acting on the oil, owing to the difference in density between the two phases. In highly permeable and steeply dipping formations, the effect of this additional force may be considerable, and it is possible for gas separating from solution to segregate up-flank while oil moves down to the producing wells. As a result, producing gas/oil ratios can be kept low, with a corresponding reduction in the rate of pressure decline, provided that all the production is taken from down-flank wells.

If there is a sufficiently large initial free gas cap, the rate of pressure decline is

small right from the start of production: the rate of evolution of gas within the oil column is correspondingly small, and can be further reduced if the gas-cap pressure is maintained by injection of surplus gas from some other source. It should then be possible to produce oil under the influence only of the gravitational head between the gas/oil contact and down-flank wells, the gas cap gradually expanding to replace the oil so removed. Under such conditions, laboratory experiments have indicated very high percentage extractions.

Unfortunately it is most commonly the case in practice that the producing rates necessary to take full advantage of the gravity effect are too low for commercial operation; at higher rates the expanding gas cap penetrates into larger channels within the oil column and drainage from the finer pores is not complete. In such circumstances, though, the presence of an initial gas cap is still advantageous. It permits of the maintenance of reasonable pressure gradients for a longer period of time, and gas moving through the partially depleted oil column may increase the recovery of oil by as much as 50 per cent of the amount obtainable by a simple solution gas drive.

The curves of Figs 5 and 6 were calculated for a reservoir of specified characteristics. From Table I it will be obvious that the recovery will vary considerably with the type of formation. Table IV, by Arps, gives computed values for various conditions, and indicates the range which may be obtained in practice. In this case the indicated pressures were taken as sufficient to dissolve the indicated amount of gas in oil of the specified gravity (and therefore vary with each example); approximate values have been estimated and appended. The economic limit was assumed to be reached when the pressure had declined to one-tenth of its initial value.

It will be noted that there is reference to fractured limestone, a type of reservoir from which much of the Middle East oil is derived. Typically the bulk of the rock has low porosity and very low permeability, but it is traversed by a network of open cracks which offers only a small resistance to flow. If such rocks were unfissured and merely exposed to the surface of a borehole, the rate of oil production would be extremely low, even with very high differential pressures. When, however, a well penetrates the fissure system, and is open to production, a low pressure is established over an area vastly greater than that normally exposed at a well bore, and very high producing rates can be obtained from a formation of extremely low permeability.

Such wells may produce initially at several thousand barrels per day (compared with a few hundred or less in many commercial sand fields), and since the fissure system permits of complete upward segregation of free gas, producing gas/oil ratios remain low and producing rates high until the expanding gas cap reaches the offtake wells. However, the rate of pressure drop tends to be low, and resistance to movement within the mass of the rock is high, with also large capillary forces. Hence, there is a tendency for much oil to be bypassed, and for the percentage primary recovery from the mass of the rock within the expanding gas cap area to be low.

The other type of natural driving force to which reference was made earlier is due to the incursion of water from an extensive aquifer; here also the effect is to reduce the rate of fall of pressure. The advancing water front pushes oil ahead of it, and since almost invariably the rock is preferentially wetted by water, water is more efficient than is gas in displacing oil. In that part of the formation

flooded by water, the amount of residual oil may be no more than 30 per cent or so of the pore space, with a corresponding percentage extraction of oil dependent on how much of the pore space was originally occupied by oil, and how much by water. Just as the effects of an initial gas cap may be augmented by the artificial injection of gas, so water is often injected below the oil water level of a reservoir in order to accelerate the natural drive, or to initiate a drive where none such would occur naturally.

The maximum possible recovery from this type of drive may be determined experimentally by resaturating a core with oil to reservoir conditions, and then forcing water through it until no more oil is recovered. The practical recovery is always less than this amount for a variety of reasons. Flow into the producing wells is convergent, with high pressure gradients in the neighbourhood of the wells, which tends to result in a relatively early breakthrough of water with subsequently increasing water/oil ratios. Similarly, in a formation of variable characteristics, water will tend to advance preferentially along the more highly permeable sections.

With progressively increasing water/oil ratios, such a field eventually reaches its economic limit, when the cost of lifting, separating, and disposing of the produced water becomes excessive. For wells of reasonably high productivity, it may be possible to handle water/oil ratios in excess of 20:1, but the practical limit varies considerably with local circumstances. These various factors will be discussed in a little more detail in the section on secondary recovery. For the moment the overall effect can be illustrated by data on recoverable reserves taken from an API report which analyses the performance of about 100 actual oilfields in an advanced stage of depletion.

Where recovery was mostly by water drive, the percentage extraction varied from 24 to 78, and the recovery per acre-foot of sand from 242 to 1165 brl. For fields reputedly produced only under the influence of dissolved gas (with gravity drainage probably playing a part in some of them), the corresponding ranges are 15 to 50 per cent and 126 to 547 brl/acre-foot. These figures indicate an overall range of about 5:1 in percentage extraction and 10:1 in the recovery per unit of sand volume, and they still do not indicate the extreme limits. Where, for example, the oil has a very high viscosity, recoveries may be less than 10 per cent and less than 100 brl/acre-foot (cf. also Table IV).

One other type of reservoir needs to be considered—that which contains gas only at relatively high temperatures and pressures. When pressure and temperature are relatively low, no particularly difficult problems are involved; but with increasing depths the problem of 'retrograde condensation' has become of importance in recent years.

Natural gas is not a pure compound, but rather a mixture of hydrocarbons the most valuable part of which consists of relatively small percentages of butane and the higher paraffin vapours. The phase relationships of such a mixture are somewhat complex in the neighbourhood of the critical point, as illustrated by Fig. 7. Thus, a mixture of point A is entirely gaseous, but if the pressure is reduced at constant temperature, some liquid is formed at point B, the amount increasing as the pressure falls to point D. Accordingly, if conditions in a gas reservoir initially correspond to A and gas is produced, liquid will be deposited within the pores of the sand and will then be trapped according to the ordinary laws of two-phase flow. One method of dealing with this problem is to

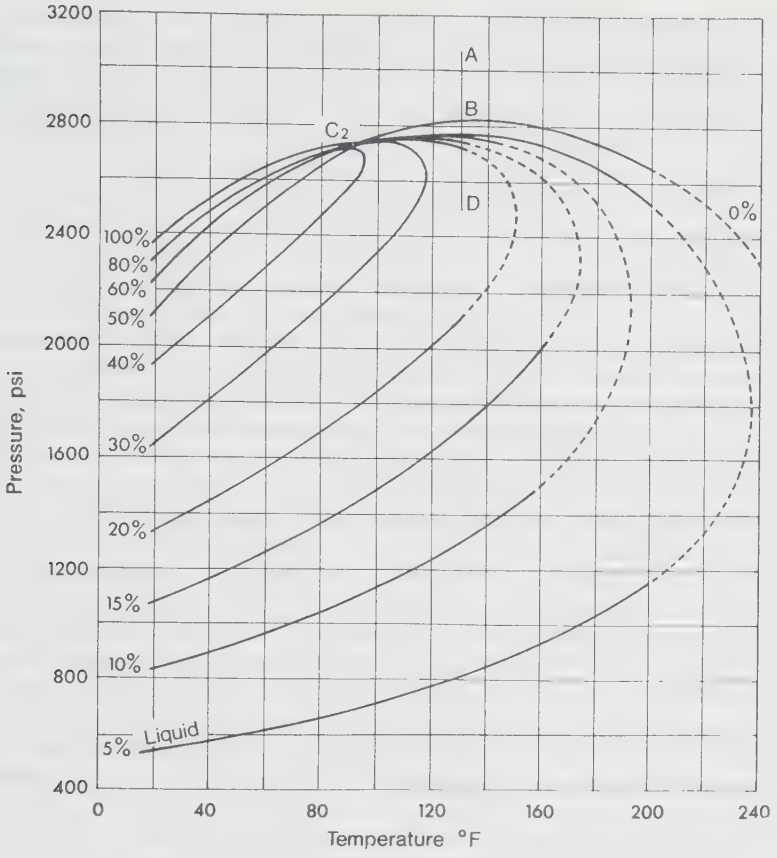

FIG. 7. Phase diagram of a natural gas–natural gasoline mixture. C_2 = critical point. (After Katz and Kurato.)

produce gas, remove it from the gasoline fraction, and to re-inject the dry gas at remote parts of the reservoir in order to maintain the underground pressure. Alternatively, the pressure can be maintained by injecting water down-flank if there is no strong natural water drive. However, when there are marked variations in permeability, channelling of injected gas to the producing wells will occur, and with pressure maintenance there is no production (other than by diffusion) from the bypassed sections of the formation. If, on the other hand, the pressure is allowed to fall, there is some production from all parts of the reservoir, and liquid deposited in the more permeable channels can later be re-vaporized by recycling dry gas.

The most satisfactory method, or combination of methods, has to be decided by detailed studies and calculations in each individual case. Thus the butanes plus content of a gas of this type may fall in the range of 25–100 brl/million cu ft and the retrograde loss in the reservoir by simple pressure depletion may be perhaps 40 per cent of this amount. Further complications may arise if there is an appreciable amount of oil below and in equilibrium with the retrograde gas.

Whether the cost of recycling is or is not worthwhile will depend on the total reserve and on the short- and longer-term markets for dry gas on the one hand and condensate on the other, and can only be decided by a complicated analysis of all the various technical and economic factors for each individual field.

RESERVOIR DEVELOPMENT

Well Spacing

One of the first questions to be decided when developing a new oilfield is the number of wells to be drilled. In earlier days it was regarded as more or less self-evident that the recovery from an oil reservoir would be increased by increasing the number of wells. From one point of view it was held that there is only a limited amount of energy available for moving oil and, by analogy with pipeline flow, the energy necessary to move oil into a well is proportional to the distance of travel. This, however, is not true of radial flow where the pressure gradients diminish rapidly away from a producing well, and it should also be clear from the earlier discussion that the work done in moving oil is far from being the most important feature of the recovery mechanism.

From another point of view, reference was made to experiments by Jamin, which indicated that when a liquid containing bubbles of gas is passed through a capillary tube, any restrictions in the tube offer an abnormal resistance to flow due to the fact that distortion of the gas bubbles is opposed by surface forces. A chain of such bubbles can withstand a considerable total differential pressure without movement, and it was thought, therefore, that the original formation pressure could only move oil over a limited distance in the case of a solution-gas drive. It is now clear, however, that although surface forces are effective, the multiple interconnected channels of a porous rock are not equivalent to a bundle of capillary tubes, and field observations have not indicated any limit to the distance over which pressure effects can be transmitted.

Finally, practical experience was invoked in support of such empirical rules as that the recovery is proportional to the square root of the well density. However, more recent analysis has indicated that such evidence is mostly adventitious. For example, if one reservoir is intrinsically more highly productive than another, there will be a greater economic incentive to drill the first reservoir to a higher well density than the second. Again, if two sections of the same reservoir are drilled to different densities, there will be a greater total producing rate from the more densely drilled area, with establishment of a pressure gradient towards it and theft of oil from the less densely drilled part of the pool. Hence, relatively more oil will be produced by wells in the more densely drilled area, but there is no evidence that the final states of depletion in the two sections will be appreciably different.

It is true that, since a field is eventually abandoned when the producing rates become too low to cover the operating costs, the amount of oil that can be extracted in commercial operation will tend to vary somewhat more with the spacing than would be expected from purely technical considerations; and where for some reason the practicable producing rates of the individual wells are abnormally low having regard to the size of the reserve, this effect may be of importance. However, in general, the consensus of technical opinion today is

that well spacing as such has no great effect on the ultimate recovery within practical limits. In practice there must be a certain minimum number of wells in order to define the boundaries and characteristics of the reservoir, and the producing wells must be properly located on structure, so as to permit control of fluid movement; clearly, for example, if a reservoir is produced by water drive, the last of the oil will only be obtained by drilling at the crest. Similarly, when the formation characteristics are very variable, attempted production from too few wells may lead to serious channelling and bypassing.

Allowing for these and other complicating factors, the minimum well density necessary for proper drainage and control is still quite commonly low, and the actual spacing adopted is determined more by the rate of production, and its effects on profits. There is always an upper limit to the rate at which a particular well can be, or should be produced. The limit is determined in the extreme case by the maximum available pressure differential, but is also affected by such factors as the 'coning' of gas or water, or the movement of sand at high differentials. There may also be a limit to the desirable rate of production of the reservoir as a whole if, for example, full advantage is to be taken of the gravity drainage effect or of a limited natural water drive. For a given reservoir then, there will be a certain minimum number of wells necessary for its development, and these will be capable of producing efficiently at a certain maximum rate. This rate can be increased up to a point, but only by drilling additional wells, and the number to be drilled has then to be determined by a balance of economic factors. On the one hand there is the additional drilling cost, and on the other the advantage of a high rate of extraction, in the form of a shorter total life, and therefore lower overall operating costs and quicker profits. These factors have, of course, always been taken into consideration, but it is clear that the estimated optimum spacing depends upon whether or not one assumes that increasing the well density leads to an appreciable increase in the percentage extraction. Accordingly the modern trend has been towards wider spacing than would have been considered advisable in the past. Some of the older fields have been drilled with one well to the acre or less, but five to ten acres per well was probably the most common density, and this may still be suitable for low-cost, high-yield wells. Under less favourable conditions spacing as wide as 40 or 50 acres per well may yield the maximum profit, while still much lower well densities are to be found in some of the fissured limestone fields, and in high-cost offshore areas.

The economic balance may be complicated by a variety of local factors, such as the availability of markets or pipeline facilities, the incidence of overheads and so on, and hence there is no single formula for determining the correct well spacing. For example, the calculation for a field whose output is limited to supplying a particular refinery differs from that of a company selling crude in the open market. Broadly speaking, the closer spacing tends to be justified in shallower formations where the drilling costs are low, in sands with high reserves per unit area, and in fields where fixed overheads are high.

The best locations for the wells are dependent on the nature of the formations and of the driving force. When there is no free gas cap or water encroachment, a uniform square or triangular pattern is commonly adopted, but this may be modified to conform with the shape of the structure and to take maximum advantage of an advancing gas or water front. It is of some importance,

therefore, to determine the type of reservoir as early as possible. The presence or absence of a gas cap is normally decided in the course of preliminary drilling, but it is not always clear whether the aquifer is large enough to provide an efficient natural water drive, and the way in which the various forces are balanced has to be determined from production experience.

Reservoirs producing only under the influence of dissolved gas normally suffer a relatively steep initial decline in pressure and hence in producing rates. Where there is a large initial gas cap, pressure and rates tend to decline only slowly until gas breaks through to the producing wells, while encroaching water may result in decline curves somewhere between these extremes, depending on how active is the drive. It is not always easy to detect a natural water drive in its early stages, particularly if there is an initial gas cap or formation of a secondary one by segregation of gas evolved from solution.

Ultimately, positive evidence is obtained by the appearance of water at what were originally clean oil wells (although even this may be due to a purely local readjustment of fluid levels within the reservoir) and confirmatory evidence may be obtainable from material balance calculations as already discussed.

RESERVOIR STUDIES AND CONTROL

The primary aim of a reservoir engineer is to obtain maximum recovery at minimum cost. Sometimes this can be achieved simply by allowing the natural forces to operate without much interference. More commonly, however, it is necessary to exercise some control and even perhaps to institute a completely artificial driving mechanism. It is quite impossible here to discuss all the possible and actual variations in detailed reservoir performance, but a few examples may be of interest.

If, for example, a very strong water drive is encroaching on a comparatively small and uniform reservoir with no gas cap, a high recovery may be obtainable simply by opening suitably located wells to production and eventually taking a high percentage of water along with the last of the oil. When, however, there is a relatively large gas cap, and in particular if the formation is not uniform, gas may break through to the producing wells before the pressure has dropped sufficiently to induce a high rate of water movement. If any considerable amount of gas is thus produced, some of the oil which is later displaced by water may be pushed into the original gas cap area. At least some of it will remain trapped there even if the water front subsequently passes through it. In such a case, therefore, it is necessary to restrict the net production of gas as much as possible, apart altogether from the effect of falling pressure on oil shrinkage and viscosity.

Again, if water advances too rapidly into a non-uniform reservoir, it will tend to flood out the more permeable sections before capillary forces can level out the water front. High water percentages or 'cuts' will be recorded at the producing wells at an early stage, and the last of the oil may be obtainable only with an amount of associated water much too high to be handled profitably. Other examples of the effect of lack of uniformity have been given earlier when talking of fissured limestones and retrograde condensate reservoirs, and there are further comments later under the heading of secondary recovery.

As a final example of the complexity of oil operations, it may be noted that not infrequently the log of a well, opposite a generally massive sand or limestone, indicates both marked variations in the characteristics of the porous formation and also interbedded thin shales. Frequently it is not easy to correlate these features from one well to another, and hence to decide whether one is dealing with several independent small reservoirs, or whether there is effective continuity throughout the porous rock with merely local obstructions.

Evidence as to continuity or the lack of it may be obtained from a study of pressure variations within the formation. Bottom-hole pressure measurements are also necessary for the material balance method to which reference has been made earlier, and which enters into the calculation of future performance, and for other purposes. Various types of instrument are available which can be lowered into a well and which record pressure variations over a period of several hours. The pressure-sensitive element is usually either a coiled Bourdon tube or bellows, and results can be obtained which are accurate to within 0.25 per cent or less of the full-scale reading, in spite of the fact that the instruments are normally less than 2 inches in overall diameter. Recently much more sensitive quartz crystal resonator gauges have been introduced whose frequency varies with the applied pressure and can be continuously recorded at surface.

Before any production has been taken from a reservoir, the pressure will only vary by the head of fluid between different levels; there may even be no measurable difference between pressures recorded in two quite distinct reservoirs after correction to a common datum. Continuity is indicated if the pressures at different places continue to agree as the normal decline sets in with production, although, on occasion, it may be necessary to design special interference tests to eliminate the possibility of purely coincidental agreement.

A major difficulty in the interpretation of these pressure records arises from the time lag in the adjustment of pressure to changing conditions; as already indicated, the pressure at the foot of a well does not rise instantaneously to an equilibrium value when flow is shut down. It is possible, however, to calculate theoretically the shape of a pressure build-up curve for various simple assumed conditions, and to use this both for extrapolating limited data and for giving information as to formation characteristics. Broadly speaking, the early rate of pressure build-up is determined by conditions in the well or in the formation near it, but after a time the shape of the build-up curve is characteristic of the average reservoir and fluid properties at some distance from the well. It may, therefore, be possible to estimate the normal reservoir permeability, compare it with that near the well, and hence obtain evidence as to the probable results of hydraulic fracturing. Similarly, the presence of a nearby fault or other barrier will be reflected in the shape of the build-up curve.

Interpretation of these curves is not always straightforward, and complications arise when two or more distinct reservoirs are connected at the same well bore. The pressure opposite each will be effectively the same in the well, but normally there will be a difference in the pressures averaged over each of the two reservoirs. This will reflect differences in natural characteristics, such as size and permeability, as well as possibly different rates of water advance or of depletion by other wells. Therefore, when such a well is shut in at surface, flow continues underground from the high to the lower pressure zone, and the shut-in bottom-hole pressure rises to a false apparent equilibrium value which is

strictly a flowing pressure. The condition can sometimes be detected by observing an abnormally low oil level in the well after shutting in at surface.

In general, a study of what is actually happening underground can only be based on pressures and rates of flow measured at the wells and interpreted in the light of the various theoretical concepts which have been outlined earlier. Even this rather limited amount of direct evidence may be confused by errors of measurement or by failure of the cement bond behind the casing. Such failure can lead to breakthrough of oil, gas, or water from some extraneous source and greatly complicate both the reservoir studies and subsequent control.

Various methods are available for checking leakage or irregular production over a long perforated interval. For example, a temperature within a well may be abnormally low or high opposite the points of entry of gas or water, respectively. The soundness of the cement bond behind a casing string may be checked by a sonic log (the amplitude of the recorded signal being relatively higher for a poor than for a good bond) and direct proof of channelling behind the casing may be obtainable by injecting a radioactive tracer.

When leakage is proved or suspected, attempts to repair the damage are commonly made by squeezing cement through perforations at high pressure, and a similar method may be used when it is desired to change the producing interval. Successful results are not always easy to obtain, and it is worthwhile to take considerable trouble to ensure that the primary cementing of the casing in place is as sound as possible. Hence, in recent years various modified cements have come into use, which are designed to give a better bond with the formation and to resist shattering when perforated.

Although far from complete, the discussion above, and in earlier sections, indicates the type of complex problems arising in the study of underground movements of fluid. Most of the methods of exercising control have also been briefly indicated. They include the choice of well locations and of perforated intervals, variations in the rate of offtake, and the deliberate injection of gas or water. The last of these is of sufficient importance to call for some further elaboration.

Secondary Recovery

It has been indicated earlier that gas or water is often injected with a view to maintaining formation pressure and achieving more efficient displacement of oil. It is desirable to consider the application of such methods as early as possible, that is to say, as soon as adequate information has been obtained as to the natural reservoir characteristics and behaviour. Justification for the necessary expense needs to be based on predicted performance curves under various assumed conditions, and some indication has already been given of the methods available for tackling this particular problem.

When gas is injected up-flank or water down-flank at a sufficiently early stage in reservoir depletion, the effect is merely to accentuate the natural driving mechanism, provided that the injection wells are located sufficiently far from producing wells. Injection of gas into a small gas cap has much the same effect as would be obtained with a very large gas cap, and injection of water below the water table similarly duplicates the effect of a very large and permeable aquifer. There is, of course, an important difference in respect of the time lag in pressure

adjustments for large reservoir volumes, but, in principle, artificial injection of this type introduces no new features.

Experiments have been carried out in which the normal direction of movement of the injected fluid has been reversed. Water has been injected into a gas cap to maintain the pressure where there is a strong natural water drive, and it has proved impossible to limit the production of gas-cap gas. On the other hand, it has been proposed to inject gas below the oil–water level in order to reduce the mobility of water encroaching into, and channelling through, a highly viscous oil.

However, of perhaps more general interest is the application of secondary recovery methods to reservoirs which have been largely depleted by natural forces. These may be reservoirs which were developed before modern techniques were used, or more modern reservoirs of low relief and variable permeability in which attempts at long-range flooding may lead to considerable bypassing of oil. In such cases, water or gas may be injected at points distributed over the entire structure, and production taken from an interlacing pattern of offtake wells.

Satisfactory results are dependent on the amount of residual oil and its viscosity, and on the local uniformity of the formation. In some cases it may be possible to plug the more permeable streaks, or when water is used, a more uniform flooding action may be obtained by delaying production until a considerable amount has been injected.

Determination of the best pattern for the injection and offtake wells involves rather different considerations, depending on whether gas or water is used. In the former there will probably be a continuous gas phase throughout the formation from the start, whereas in the latter, oil will tend to bank up ahead of the advancing water. For water, the most common pattern is the 'five-spot' with injection at the corners of a square and offtake from the centre, but in any particular case it is necessary to balance the costs against the additional recovery expected. Even floods of this nature can leave considerable quantities of oil in the formation, and may be quite uneconomic if the oil is very viscous.

In laboratory experiments with linear flow of water into an oil-saturated core, the greater part of the movable oil will be displaced before any water breaks through at the outlet. Further oil production can then occur at high and increasing water cuts until the residual oil is down to the irreducible minimum. In the field, however, various complications arise. In the first place, we are dealing with radial flow out of and into wells, with a concentration of pressure gradients around the points of input and offtake. The shape of the advancing water front is distorted, and breakthrough of water occurs before the whole of a particular spacing unit has been flooded. This behaviour can be calculated for systems of simple geometry, but can also be illustrated by an electrical analogue. For example, the formation can be simulated by a gelatine film rendered conductive by zinc ammonium chloride, the 'wells' being electrodes encased in a copper ammonium chloride gel. Movement of the ions in the model and hence, by analogy, of the water front in a water drive, is then indicated by the progressive spread of a blue coloration away from the electrodes corresponding to the injection wells. Figure 8 is an example of the results of applying this method to a five-spot pattern, and indicates only about 70 per cent of the area flooded by water before breakthrough occurs.

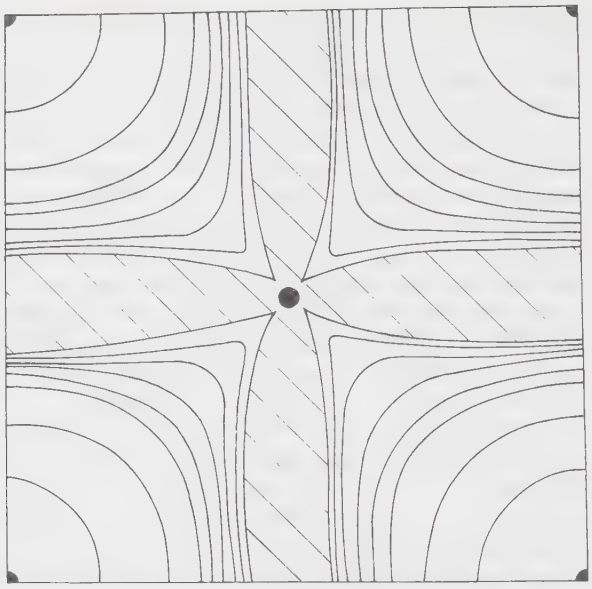

FIG. 8. History of injection fluid front in a five spot system (from an electrolytic model). The heavy lines indicate the shape of the front at various times with injection at the corners of the square. The hatched zone is not swept out at the time of breakthrough to the control well. (After Wyckoff, Botset and Muskat.)

In the field there is the further complication arising from the fact that the viscosity of the oil is often much higher than that of water, and in particular the ratio k_o/μ_o is much lower than k_w/μ_w, where the first applies to flow in the unflooded area ahead of the water front, and the second to flow behind it. This unfavourable 'mobility ratio' results in a lower sweep efficiency to breakthrough in a uniform sand, and also tends to accentuate any perturbation of the water front arising from local irregularities.

Finally, there is the question of permeability stratification. If there are strata of different permeabilities which are continuous between injection and offtake wells, injected water will more easily enter the more permeable sections with earlier breakthrough, and in consequence the produced water cut will rise in a step-wise fashion (as less and less permeable strata are flooded) at a much lower cumulative oil recovery than would have been the case for a strictly uniform sand.

Computation of the performance of a water flood is an extremely complicated procedure if any attempt is to be made to take detailed account of all the various factors which can influence the results (such as, for example, cross flow between strata of different permeabilities), and cannot be discussed in this brief article. Calculations based on much simplified models and assumptions as to the physical processes involved may under favourable conditions, give a reasonable forecast of the general trend of the water/oil ratio and production curve. The Stiles method, for example, is based on linear flow, equal mobilities for oil and water, no cross flow between beds of differing (assumed known) permeabilities, with all of these beds having the same porosity and relative

permeability characteristics. With these assumptions and a constant rate of water injection the water will be distributed between the various strata in proportion to their permeabilities, and if it is further assumed that at breakthrough there is an abrupt change from 100 per cent oil to 100 per cent water in the effluent stream, the times of breakthrough in each bed can be calculated from the amount of displaceable oil in it.

At any time the produced water/oil ratio can then be calculated by taking the flow of water as proportional to

$$\frac{k_w h_w}{\mu_w}$$

and of oil to

$$\frac{k_o h_o}{\mu_o}$$

where h_w and h_o are respectively the millidarcy-feet carrying water and oil at the producing well.

In any event there is commonly sufficient uncertainty as to the detailed characteristics of a reservoir to justify a pilot test in a small part of it before proceeding to a full-scale plant, and various operational matters need careful consideration. For example, the injected water must be compatible with the natural formation water and not lead to swelling of any clay content there may be; frequently also it will need treatment to inhibit bacterial growth; excessive injection pressures may lead to parting of the formation along bedding planes, and it may be necessary to modify the well pattern to take account of formation dip or anisotropy.

Under favourable conditions a well-planned water flood can result in a very considerable increase in the oil recovery over that obtainable by a simple solution gas drive. There are, however, many factors which can militate against the obtaining of successful results. In particular, when the oil viscosity is very high and the mobility ratio therefore unfavourable, the sweep efficiency of a flood can be very low, with the result that produced water cuts rise to uneconomic values before substantial additional recovery has been obtained. Various attempts at improving the efficiency of such floods or devising alternative techniques have therefore been made.

Enhanced Oil Recovery (EOR)

Sweep efficiency may be improved by increasing the viscosity of the injected water with the addition of a high-molecular-weight water-soluble organic polymer such as partially hydrolysed polyacrylamide. Removal of residual oil may also be improved by adding a surfactant (such as an organic sulphonate) to reduce surface tension. These additions tend to be expensive and their effectiveness may be reduced by adsorption on to the sand surfaces. For these and other reasons (including the availability of alternative EOR methods) chemical floods have not yet been very widely adopted. In mid-1982, for example, only about 100 were reported in the United States, many of them small pilot projects. At this time a survey by the *Oil & Gas Journal* reported

374 948 b/d of production in the USA by various EOR methods, of which only 4409 b/d came from the use of chemical additions as described above. The greater part of the total (296 629 b/d came from thermal stimulation of heavy oil reservoirs, most commonly by injecting steam). Broadly speaking there are two variants. The 'huff and puff' or steam-soak method involves alternating periods of steam injection and oil production from the same well. Benefits are obtained by cleaning out wax or asphalt deposits, and hence improving permeability and also by lowering the viscosity of oil entering the heated zones around the well bore. There will be a limit to the number of cycles that can be advantageously used, and this process may then be followed (or entirely replaced) by a conventional drive with separate injection and offtake wells as in the case of a water drive. With steam the displacement process is much more complex than in the case of water. As steam advances into the formation it will condense to give a liquid water phase driving oil ahead and itself being driven by steam. In the heated zone, volatile components of the oil may be evaporated and otherwise the specific volume of the residual oil will tend to increase and its viscosity to diminish greatly. As with water, the steam drive performance will be affected by channelling, permeability stratification and the like, but account has to be taken of the fact that some heat will be conducted into areas of the formation not directly contacted by steam, while in some cases the sweep efficiency can be materially improved by adding foaming agents which plug the oil depleted zones promoting the entry of steam into undepleted intervals. The process tends to be expensive, largely because of the cost of fuel used in steam raising, but in favourable circumstances has resulted in yields of 50 per cent or more from reservoirs which by more traditional methods would not have been expected to yield as much as 10 per cent.

An alternative method of heating the formation is that of *in situ* combustion; air is injected into the reservoir and oil in the immediate neighbourhood of the injection well is ignited, the flame front moving towards producing wells. Evidently this process has some features in common with the steam drive. However, the steam produced is diluted with nitrogen and carbon dioxide and some cracking of oil is likely to occur. In the area swept by the flame all the oil is removed and it is possible to apply the method to reservoirs which have been largely depleted by other methods. However, the sweep efficiency tends to be very poor and although currently a few projects of this type are being operated, steaming seems to be the generally preferred method of thermal stimulation.

Other EOR methods are mostly variants of the 'miscible drive'. Displacement of oil by water is incomplete, basically because of surface forces at the interface. A light hydrocarbon which is miscible with crude (such as liquid propane) will displace effectively all the oil in its path, but is normally too expensive to use as a complete flooding agent. However, if a slug of propane is followed by gas at a high enough pressure, the propane is miscible also with the gas and will itself be effectively displaced. At still higher pressures injection of gas alone can form a miscible fluid front if the residual oil has a high enough content of light fractions.

A variant which has received increasing attention in recent years involves the injection of carbon dioxide to swell the oil and reduce its viscosity and surface tension at the flood front. Carbon dioxide also is generally not cheap in pure form and large quantities, and its high mobility tends to lead to early

breakthrough at producing wells, and various methods have been tried in an attempt to improve the sweep efficiency, as, for example, by the intermittent injection of water.

In the space here available it is not possible to do more than outline the more important EOR methods since theoretical calculations are clearly much more complicated than for primary and normal secondary recovery processes. For example, variations in the composition of the vapour phase may have little effect on primary recovery, but are clearly important in miscible drives, while temperature variation and the conduction of heat are factors which need to be considered in thermal drives; some indication of the methods of analysis of these problems may be obtained from Reference 6.

CONCLUSION

In earlier editions of *Modern Petroleum Technology* this chapter contained a brief discussion of methods available for lifting oil from the foot of a well and treating it at surface. These topics are now discussed in greater detail elsewhere. So far as the main topic of this chapter is concerned, it is still true that a large fraction of all oil discovered is left in the ground. In North Sea fields, for example, percentage recoveries in the range of 40 to 50 per cent are commonly predicted. Active research (both theoretical and experimental) aimed at increasing such yields has been greatly stimulated by the large increases in oil prices over the last ten years, and it would not be unreasonable to expect that significant improvements in such recovery factors will be possible in the future.

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6

Production of Oil and Gas

By P. SELWOOD

PRODUCTION may be considered as that section of the oil industry concerned with conveying hydrocarbons from the reservoir to surface, and the separation of oil, gas, water, and entrained solids to the extent necessary to provide a saleable primary product such as crude oil, NGL (natural gas liquids), and gas.

For any given oilfield the commitment to the type of production facilities, both within the well bore and at surface, will be based on data obtained and analysed from the initial discovery well and subsequent appraisal wells. Data directly obtainable from the wells include the following:

1. Crude oil quality.
2. Volume of associated gas and its quality; the presence of hydrogen sulphide as a constituent having serious engineering, safety, and economic implications.
3. Reservoir pressure, and the resultant closed-in wellhead pressure.
4. Relationship between rate of flow of the crude oil and drop in both reservoir pressure and wellhead pressure.

Other data obtainable from the wells such as reservoir depth and thickness, rock permeability and porosity, in some cases gas/oil or oil/water contact will be combined with other geological information to develop a picture of the reservoir. Using these data the reservoir engineers will calculate the amount of oil contained within the reservoir rock and the percentage of this oil that they believe to be recoverable. They will develop a series of scenarios predicting the way the field would behave as the oil is produced. These may include reinjection of produced or other gas or water to help to maintain the reservoir pressure. This injection may be commenced to coincide with the start of production of the oil, or visualized as occurring after a specific period of time or volume of oil produced.

For some or all of these predicted scenarios an economic evaluation will be made and then a decision taken on the production plan, from which come the number of wells and size and type of production facility. Elsewhere in this volume reservoir engineering and geology are dealt with in greater detail. Mention of them in these introductory remarks on the production of oil aims to emphasize the link between the predictive processes of the reservoir engineering team and the physical equipment used in the development of an oilfield.

GENERAL CONSIDERATIONS ON OILFIELD DEVELOPMENT

With the increased emphasis on the development of offshore oilfields throughout the world, and particularly off the coasts of Norway and Great Britain, one very significant difference between onshore and offshore development is worthy of note. Examination of the development of the major

onshore oilfields of the Middle East will reveal that the early development decisions were cast-iron certainties. Production started with a small number of wells, a production facility, and relatively small pipelines. After some years of production these facilities were expanded and, in some cases, expanded yet again after a further period of production and knowledge that the original predictions were soundly based, or suitably modified to suit the past field performance.

Offshore, especially in the deep (300–600 ft) waters characteristic of the North Sea fields developed in the last decade, such leisurely development and comparatively risk free decisions are not possible. The reason is the necessity offshore to build a platform to house the production facilities, and normally all of the wells. Such large platforms cost hundreds of millions of pounds. A small platform would be comparatively more expensive, since it would have to be built to withstand the same environmental forces as a large one; 120 miles an hour winds and 100-ft waves. Similarly, the primary influence on the cost of offshore pipelines is the lay barge, not the pipe size. The decision offshore, especially in deep water, is characteristically one to install all the production facilities and any pipelines deemed necessary for the ultimate development and maximum production rate of the field *before* limited or pilot production has taken place. The risks involved in taking such a decision are probably orders of magnitude higher than those taken at such an early stage in development onshore.

Part of the field development decision will be the number of wells required and the volume of crude oil they are required to produce. Similar decisions will have been made about gas and/or water injection. All of these decisions are the basis on which plant is ordered.

Onshore typical development will have wells drilled vertically to the reservoir. Flowlines will go back to a centrally located production facility where adequate separation between the elements of the production facility may be maintained. These are described in more detail later, but may include gas, oil, and water separators; pumps to handle gas or water injection into the reservoir; storage tanks and export pumps and pipeline. Neither the weight nor dimensions of this equipment, nor those of the drilling rig used at the well sites are of critical importance.

Offshore the details of weight and dimensions must be agreed very early in the development plan. All, or much of this plant, must be supported above the water by some form of structure. This cannot be designed until the required dimensions of the working deck or decks, and dead and dynamic loads have been nominated.

North Sea development will be used to illustrate the options available and decisions required before the structure to hold wells and production facilities can be designed.

In the Southern Basin gas fields off Yarmouth, in up to 150 ft of water, a number of structures joined by walkways are used. The structures house wells, production facilities, personnel and, if necessary, compressor plant. Using this approach allows drilling to be commenced ahead of construction of the production facilities. This can reduce the time span between financing the production facilities and their use to generate income. It also separates drilling and production in a fashion similar to onshore operations.

In the next phase of development, mainly in the Central oil producing area, with up to 400 ft of water, a variety of approaches have been used. Developments using both the above separation of drilling, production and accommodation, and designs in which they are integrated on the same platform have occurred. One field was developed using a floating production facility with subsea wells. This, as with the use of a separate drilling platform, allows the financing of the production facilities to be better phased than is possible with an integrated platform where no drilling is possible until the jacket, deck, and most facilities have been installed.

Some of these fields have pipelines to shore so that production is independent of weather. Others have offshore loading facilities, often Single Buoy Moorings (SBM), a mile of so from the platform to which tankers can tie. With only one SBM production must be intermittent while tankers change over, and it is also weather-sensitive. With two SBMs production is still weather-sensitive, even if a tanker is theoretically always available. Some platforms have been built with oil storage facilities, and this can be used to smooth out production to a significant extent.

East of Shetlands, in up to 600 ft of water, the massive bottom-supported integrated platform, consisting of jacket, deck, and facilities, was the standard approach in the late 1970s. Pipelines or offshore loading with or without oil storage are all to be found.

More recent developments have shown the industry to be investigating methods of reducing costs both in absolute terms and also by reducing the front-end loading, the time between financial expenditure and generation of income. At the same time, many of these developments are concerned with techniques to allow economic development of oil in more than 1000 ft of water.

One means of reducing front-end loading is to drill the wells, or at least some of them, before installing the production platform. Individual subsea wells achieve this. Template drilling, where a number of closely-spaced wells are drilled by a mobile rig before installing the platform over them, is being used as an attractive variant. It avoids the possible flowlines and control lines damage on distant subsea wells that has occurred through trawling activities.

Another approach being examined is to install the production facilities on a tanker. The tanker may then tie on to a suitable SBM or equivalent, linked directly to a subsea well.

Bottom-supported structures in 600 ft of water are extremely expensive. Floating facilities using the sea rather than combating it have obvious advantages, and if one could ignore tethering problems would scarcely be depth-sensitive. Unfortunately, as we require to bring pressurized hydrocarbons from the sea-bed to the production facility tethering is a very serious problem. Semi-submersible drilling rigs with catenary anchor systems are being used, but they have horizontal and vertical motion which has to be allowed for in the design of pipework.

A vast array of proposals for allowing the platform to be bottom tethered, use the buoyancy of the sea, but to move with it to a controlled degree have been made. One example is being installed in the North Sea. This is a Tethered Leg Platform (TLP). This 'floating' unit is held by vertical anchors and is pulled down to tension the anchor lines. This buoyancy-created vertical tension will generate a horizontal component if the unit moves off centre and thus limits

such movement. With this method, and many of the other designs, horizontal motion remains, but vertical motion is effectively eliminated.

The above summary of North Sea offshore development illustrates some of the options and decisions required. While the wells and production facilities offshore are similar in principle to those onshore their deployment will depend on the layout of the platforms.

WELL COMPLETION

Turning to more specific aspects of production Fig. 1 illustrates schematically some of the well completion types found. Figure 1(a) represents the simplest completion, and one occasionally found. This has casing cemented into the hole above the reservoir. The well is then deepened into the reservoir, the drill pipe and bit removed, and the well produced. This type of completion is commonly known as a barefoot completion, because the reservoir is exposed and, of necessity should be self-supporting. The difficulty with this type of completion is that while drilling the well must be filled with a column of mud of sufficient weight to prevent the oil flowing from the reservoir. On completion it is possible to bale out the mud, lowering the column height and thus the pressure, until flow of oil commences. This practice is dangerous, because the well may flow abruptly and violently, while the bailer or swab on its cable is down the well bore.

The normal solution to this problem is to suspend a further string of pipe, called tubing, inside the casing and this is illustrated in Fig. 1(b). Typical tubing sizes are $2\frac{3}{8}$ and $3\frac{1}{2}$-inch diameter, inside 7-inch casing. Having completed the well the drilling mud can be circulated out by pumping a lighter

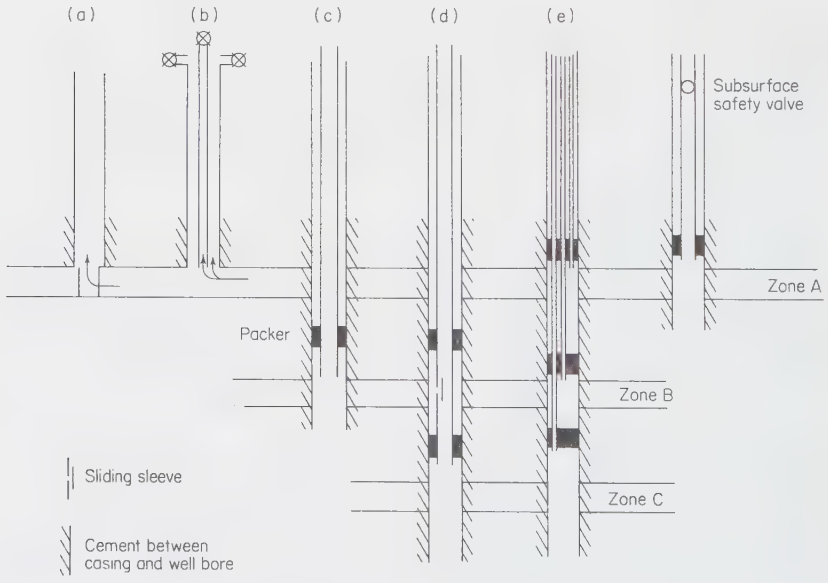

Fig. 1. Types of well completion.

fluid down the tubing and allowing it to return to surface via the tubing/casing annulus. This lighter fluid can be water, crude oil, or even a gas. Such a type of completion has a further advantage. It may be necessary to revert to the status of having the well full of a mud to allow further work to be carried out using a drilling rig. With tubing in the hole pumping in mud and circulating out the oil and gas achieve this safely and rapidly. In oil industry terminology this is killing the well for a work-over.

Formation Damage

There is another advantage in such a completion if it is necessary to remedy completion damage. Such damage can occur for the following reasons. When a well is being drilled, one of the desirable characteristics of the drilling mud is its ability to seal off porous and permeable formations. The intrusion of bentonitic clay particles, starches, and carboxymethylcellulose, commonly used in drilling mud as sealants, into the void spaces of the rock or their coating the surface of the well bore achieves this objective. However, the intrusion of solids into the rock can reduce the permeability. As the mud cake is being formed liquid mud filtrate penetrates the walls of the well bore. This fluid can cause swelling of any interstitial clays forming part of the reservoir rock itself. Also, purely by increasing the water content of the reservoir rock, it can reduce the relative permeability of the rock to oil.

The combination of the above effects, enhanced further in many cases by that of the cement slurry used in wells where casing is cemented through the reservoir rock, is to reduce the rock permeability close to the well bore to a greater or lesser extent. This damage to the reservoir rock close to the well bore is critical. If one considers the flow into a well it is readily apparent that the fluid flow rate across any circular boundary centred on the well bore is inversely proportional to the distance from the well bore, i.e. the fluid is moving imperceptibly at a distance from the well bore and at a high velocity as it enters the well. Thus the damage near the well bore is in an area where the oil is required to move at its highest velocity. This damage is often quantified in terms of an additional pressure drop per unit of flow and called the skin effect.[1]

Formation Stimulation

With tubing run to near the bottom of a well it is readily possible to circulate a remedial fluid to the bottom of the well and then by closing the surface valves continue to squeeze it into the formation. This fluid can restore the permeability or increase it above that originally present. Hydrochloric acid at 15–30 per cent strength, suitably inhibited to reduce the degree of attack on the steel casing or tubing through which it has to pass, is commonly used on limestone reservoirs. At low pressure it penetrates and dissolves the rock near the wellbore, while used at high pressure it is primarily employed to generate enough force to fracture the rock hydraulically, and then it etches the resultant new surfaces to leave an enhanced flow path when pressure is released and the fracture closes. For sandstones, hydrofluoric acid and a variety of surfactants are used to clean up the damaged rock. An alternative method is to use a fluid, normally water-based, to fracture the rock hydraulically, the resultant fracture being propped

open with sand, glass beads, or other suitable agents entrained in the injected fluid. It sounds a simple idea, but debate over whether the fractures are vertical, horizontal, random, or by some techniques directionally controllable, continues. Similarly, transport of sand by a fluid along the fracture appears simple, but, by definition as a reservoir rock, the sides of the fracture are permeable. The fluid leaks away and a sand particle traffic jam results. The ideal fluid must temporarily seal off this porosity while pumping, and then change character so that the seal is subsequently removed. Fluids of this type have been developed.

In the two examples, Figs 1(a) and 1(b), the casing was set above the reservoir. A more normal completion would run the casing through the reservoir and cement the casing in place. This helps to prevent friable reservoir rocks collapsing into the well bore. It also allows selective production from the reservoir and subsequent isolation of zones that produce excessive water or gas.

Multiple Completions

Figure 1(c) shows a completion where the casing has been cemented through two zones and the tubing is packed off at the bottom so that zone A flows through the annulus and zone B through the tubing. In this type of completion the casing is perforated with a shaped charge. This is an explosive charge within a hyperbolic cone so that when it is detonated electrically the explosion is focused to burn a carrot-shaped hole through casing and cement and into the reservoir rock. Such 'guns' can be run through tubing and retrieved with pressure on the well. For zone B it would be easy to use this method, with the tubing filled with a fluid exerting less pressure than the reservoir pressure, so that oil flows into the well immediately the casing is perforated, rather than face the prospect of mud flowing out into the reservoir and the perforations inducing further reservoir damage if the casing is perforated with an overbalancing fluid. Zone A would normally have to be perforated with an overbalancing mud in the hole to allow the tubing and packer to be run subsequent to perforating.

Figure 1(d) shows a style of completion with two packers and a sliding sleeve (controlling ports or orifices) capable of being opened and closed by wire-line tools from the surface so that zone B or C, or both comingled can flow on the tubing. Figure 1(e) shows a technically more complex completion with all three zones flowing independently in separate tubing strings. A variant on this approach is not to put casing in the well, but to cement the three tubings into the open hole. In effect this is reverting to Fig. 1(a), but with three wells on the same location. The most interesting technical development that had to be undertaken before this technique could be adopted was one to allow perforation of one tubing without shooting holes through the adjacent strings of tubing.

Safety

Offshore wells are completed to flow on tubing only, with a subsurface safety valve in the tubing string well below sea-bed. For the high-volume North Sea wells 5-inch tubing is common. Subsurface safety valves are fail safe, often held open by pressure transmitted to them from the surface with a powerful spring

trying to close them. A drop in the pressure, and thus closure of the valve, can be induced by production monitoring equipment, fire detectors, etc. Few onshore wells are completed in this way. They are not grouped on platforms in close proximity to one another, with all the production facilities and, on a large North Sea platform, living quarters for 300 men. Another consideration is the widespread oil slick which might develop if control of an offshore well is lost.

The type of completion discussed above, and more complex ones, are all to be found. There are a number of factors considered by the operator when deciding on the completion type. The offshore operator has a narrower range, since he requires a subsea safety valve which normally restricts him to tubing flow. Subsurface safety valves operating on the annulus have been produced, but are not in common use. For the land-based operator the more complex completions are available. However, the more complex the down-hole equipment the higher the probability of either equipment failure, packers or sliding sleeves leaking, or problems developing during wire-line manipulation of this equipment. Such failures may well require the well to be worked over, and killing a well thoroughly cleaned up by subsequent production with any overpressuring fluid has a high probability of damaging the formation and causing irreversible formation damage. The required well production rate will have a marked influence on the completion technique. Few wells are completed with casing larger than $9\frac{5}{8}$-inch, and 7-inch is perhaps more typical even for high rate, 10 000-bpd, Middle East or North Sea wells. With the $3\frac{1}{2}$-inch tubing commonly used inside 7-inch casing such high flow rates may well be unobtainable on tubing flow alone. In the USA where 100 bpd may well be the regulatory allowable rate of oil production the use of multiple strings of small diameter tubing can be made since the dimensions of the vertical flow path are not a primary influence on the rate of oil production obtainable.

Although complex completions may cause work-over operations, at times they may also be instrumental in reducing the need for them. In Fig. 1(d), for example, should zone B or C, after a period of time, be producing unacceptably large volumes of water, then wire-line manipulation can be used to isolate the offending zone.

WELLHEADS

At surface the wellhead of a flowing well consists of an arrangement of valves. For high-pressure wells, and pressures above 5000 psi are not uncommon, there would normally be a 'master gate' on each flow path, to be used only in emergency, or to isolate and allow repair or replacement of the next or operating valve. Downstream of these operating valves will be a choke, either fixed or in the form of a solid metal cone that can be moved into an orifice to allow variable flow rates. In the latter case a 24/64-inch setting means the cone has been moved into a 1-inch orifice (64/64 inch) to leave an annulus equivalent to a 24/64-inch diameter hole.

Beans

At any particular time, the actual oil-producing rate of a flowing well is dependent on the overall pressure drop and on the resistance to flow in the

formation, in the tubing, and at the surface. Positive control of the rate is normally effected by the beans or chokes inserted in the flow line at the wellhead. Provided that the back pressure against the choke is less than about 60 per cent of the tubing-head pressure upstream of it, flow through the orifice is similar to critical flow through a steam jet and is not affected by fluctuations of pressure downstream in the surface installations.

The precise calculation of choke capacity involves data which are not usually available, but the following approximate formula is satisfactory over moderate ranges of the variables:

$$\frac{Pd^2}{V\sqrt{G}} = C$$

Here P is the upstream (tubing head) pressure (psi); d is the choke diameter (1/32 inch); V is the oil throughput (bd); G is the gas/oil ratio (cu ft/brl); and C is a constant the magnitude of which varies somewhat with the oil density and other local conditions, but has usually only a small variation for wells producing from a given reservoir. The mean value falls within about the range of 3.5 to 4.5. Theoretically, more exact formulae can be derived but, having regard to the normal range of errors in field measurements, the ratio quoted is convenient and useful if its limitations are borne in mind. It permits of spotting gross errors of measurements, plugging or cutting of the choke orifice, and the development of excessive back pressure, as well as of estimating approximate values for data which for one reason or another have not been recorded.

REMOTE CONTROL, ETC.

The illustration, Fig. 2, is of an offshore well flowing on tubing only. Many wellheads are made in this way by assembling individual parts using nuts and bolts to provide the required system. To save weight, eliminate many sources of leakage and to speed assembly, modern wellheads may have unitized blocks containing more than one valve. For subsea wells, as a matter of necessity to avoid the need for divers to open and close wellhead valves, all or some of the valves are power-operated by remote control. With all platform wells closely grouped, and near the control room, powered remote operation is also commonly used, in this instance as a matter of operational convenience.

In the same way that remote operation of wellhead valves is a necessity for subsea wells there was a need to develop methods of running and manipulating wire-line tools, such as the gas-lift mandrels, subsurface safety valves and sliding sleeves already mentioned. Two approaches have been taken. In the first the subsea wellhead is fully enclosed so that the internal pressure can be reduced to atmospheric when required. Because of the possibility of release of hydrocarbons into the very limited area within the chamber, water or an inert gas has been used rather than air as the work environment. The wire-line equipment and operating crew are taken to the well in a diving bell, lock on, reduce the well container to atmospheric conditions and, except for the need to wear breathing apparatus and the restricted space, the crew then operate their equipment as if on the surface.

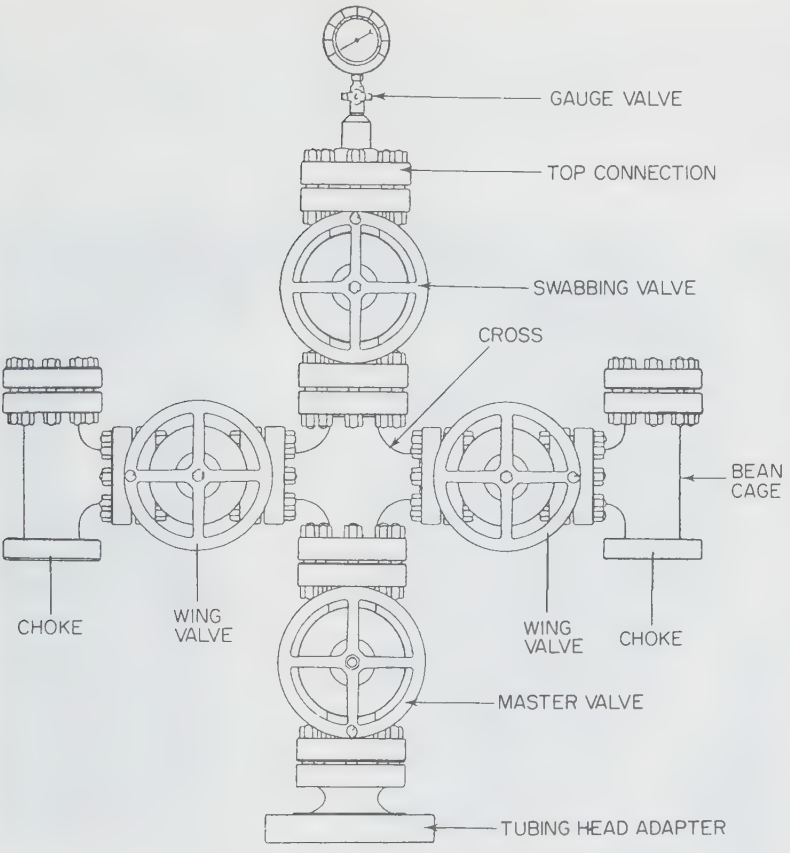

Fig. 2. Typical Christmas Tree.

Through Flowline System

In the second approach the 'wire-line' tools are manipulated from the surface without wire by pumping them in and out of the wells. This TFL, through flowline system, demands a double completion so that the tools may be pumped both in and out. The flowline tie-in becomes more complex, with two flowlines and an annulus access line. Similarly, the control design becomes more complex as the number of operating valves increases. Visually the most striking characteristic of a TFL wellhead is the sweeping curve of the flowline from sea-bed level to the top of the well, essential to allow tools to be pumped, as illustrated in Fig. 3.

The system is already showing great promise and has been adopted for the Underwater Manifold Centre to be installed in the North Sea. This will house a number of wells with TFL capability. The centre is also designed so that most maintenance of the complex can be carried out without diver assistance, using an RMV (remote maintenance vehicle). The prime bonus from success with this type of production system is the prospect of extending production

capability beyond 1000 ft, near the economic limit of fixed platforms and the physical limits of diver intervention.

Some wells produce formation particles, normally sand grains, with the oil and gas, and a detection device is often fitted in the choke to warn that this is happening. In a high-volume and thus high-velocity well it is essential to detect

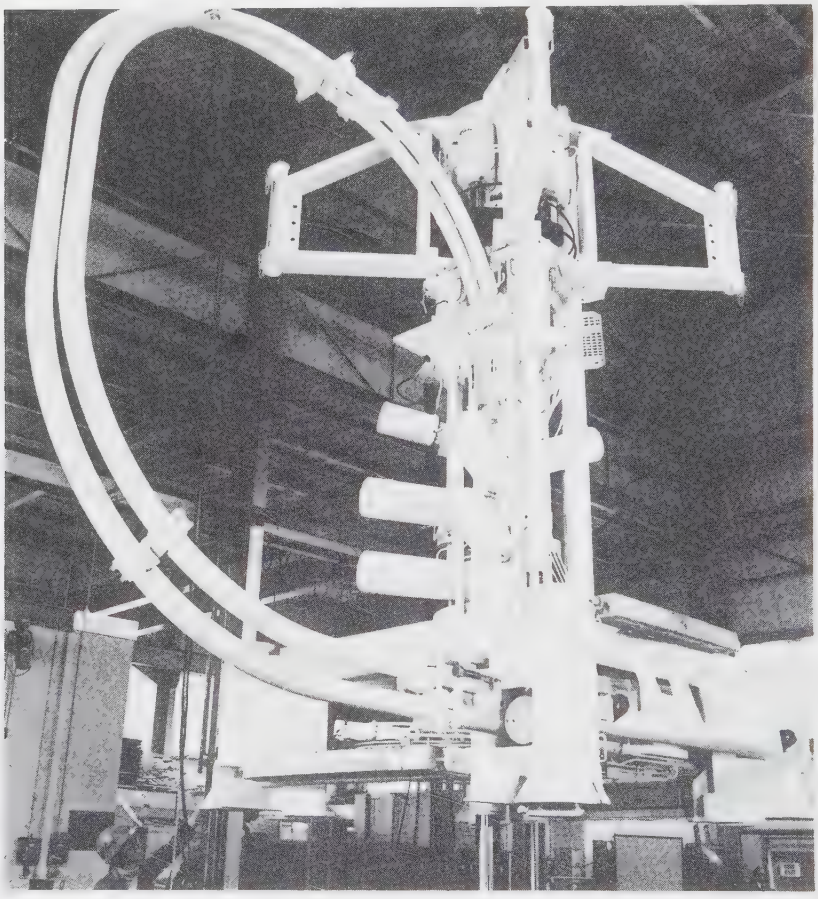

FIG. 3. Through flowline wellhead. (Photograph courtesy of McEvoy.)

this sand flow very soon, because it can readily cut through the metal and cause loss of control of the well.

Other problems with well flow can arise from the characteristics of the oil. Some precipitate asphaltenes or wax as they flow up the well bore. The resultant deposits can cause operational difficulties in the well bore or downstream separation facilities. In some cases chemicals injected into the flow stream are used to control the situation. In others tubing may have to be scraped *in situ* or removed and cleaned out periodically.

NATURAL FLOW IN A WELL

Before discussing the methods adopted to assist the flow of oil to surface within the producing well it is worthwhile to examine the mechanisms that occur in naturally flowing wells. The quantity of gas associated with the oil is commonly expressed as cubic feet per barrel of oil. In the North Sea 100 cu ft/bbl is common but it may run up to 1000 cu ft/bbl, or approximately 20 to 200 volumes of gas/volume of oil. For the crude described in Fig. 4, if the wellhead pressure were 700 psi and 75 per cent of the gas has come out of solution the volume ratio of free gas to oil in the well bore will range from 0.3/1.0 to 3.0/1.0.

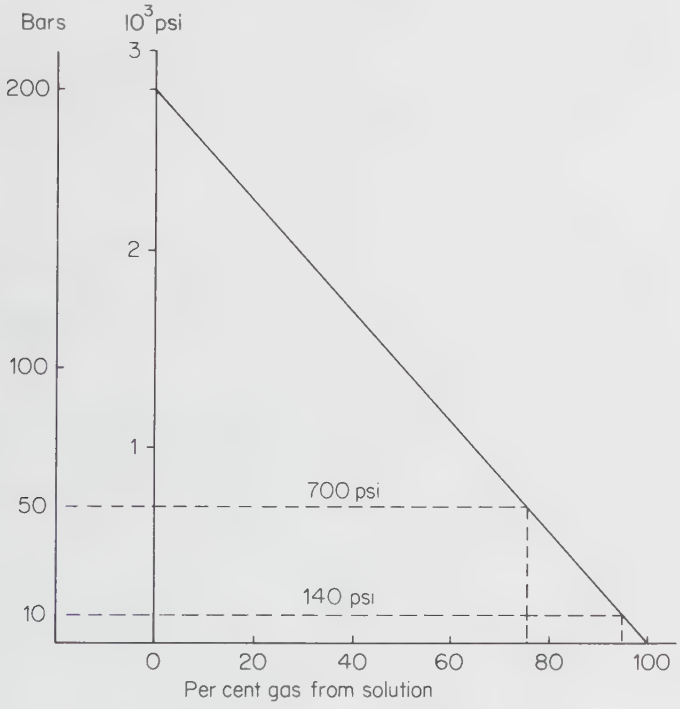

Fig. 4. Gas release versus pressure.

For the example reservoir oil the vertical flow would be undersaturated crude until the pressure drops to 2800 psi. Bubbles of gas then start to form, randomly distributed and of random diameter, at 2800 psi (200 bars). The bubbles will move at different velocities, dependent on their respective diameters. The oil will be affected by drag where it is in contact with the tubing or annulus wall, but otherwise moves at a fairly uniform velocity.

The next stage is slug flow where the bubbles have coalesced to form stable bubbles whose diameter approximates that of the containing pipe. The bubble velocity will be higher than that of the oil. The oil away from the bubble in the slug, will be moving in the direction of the bubble, but the oil film around the gas bubble may be moving down the surface of the bubble.

The final stage is mist flow when the gas has become the continuous phase and the oil is in the form of entrained droplets. The transition from slug

flow, with oil the continuous phase, to mist flow, with gas the continuous phase, does not occur instantaneously, and is an added and ill-defined region that may be found in the well bore. For the example well described above mist flow may occur near the surface at the 3.0/1.0 gas volume to oil volume ratio, but is improbable at the lower ratio. Thus, for the example well with a bottom-hole pressure above 2800 psi single-phase, bubble slug and mist flow may all be present at various points in the vertical flow stream. A large number of methods have been proposed to predict two-phase pressure drops in flowing wells, and a number of these were evaluated by J. Orkiszewski.[3]

ARTIFICIAL LIFT

In most oilfields reservoir pressure decline and increased volumes of water produced with the oil give rise to conditions where the wells will not flow unaided. A number of options are open to assist oil flow to surface.

Gas Lift

One method is gas lift. In this method gas pumped down the annulus is introduced into the flow stream via pressure-controlled valves placed in the tubing string. The expansion of this gas as it rises helps to lift the oil. The gas can then be recovered and if necessary, recycled via compressors to provide the additional energy needed to lift the oil.

Stated in these simple terms it ignores a great deal of the engineering expertise needed to make the method work satisfactorily. The sizing and location of the valves call for a knowledge of the required oil flow rate and the quantities of associated gas. When the well is flowing some gas will be produced with the oil. Following well shut-down, however, the initial oil may be effectively dead, its gas having escaped to surface with the well bore acting as a separator. One of the two-phase gradient curves, based on theoretical visualizations of the vertical flow path, will be used to size these valves, and that of Duns and Ros[4] is frequently employed in modern computer programs.

The valves inserted into the tubing are often wire-line retrievable and may be fluid or pressure operated. They may also be proportional response throttling valves, with gas throughput from annulus to tubing directly proportional to the flowing tubing pressure. With this kind of valve the upper unloading valves are closed by the reduction in tubing pressure as gas is introduced through the next lower valve station. Using these sophisticated valves achieves maximum depth of injection with minimum gas/oil ratio.

Gas lift is a very flexible method, well adapted to the deviated wells common in offshore operations, and rapidly adjustable to both changes in required production rates and changes in character of the produced fluids. The rise in water content with time, common in many wells, has clearly a significant effect on the pressure system within the well bore.

Slippage of the gas through the oil is one cause of inefficiency in gas-lift operations. Another type of gas lift attempts to combat this by placing a free moving piston between oil and gas, with the tubing string as the cylinder. This is an intermittent type of gas lift, because when the gas has pushed the piston and oil up the hole, the piston must fall to the bottom to repeat the cycle. As

with the previous method surface pumps, or an alternative source of high-pressure gas, are used to transmit energy in the form of gas into the well bore and help to lift the oil. This method is not very suitable for deviated wells and is little used today.

Subsurface Pumps

A third method, commonly used in high-volume wells, is to lower an electrically-driven multi-stage centrifugal pump into the well. This converts electrical to hydraulic energy within the well bore. These pumps have been used extensively in vertical shallow (and cool) wells, but require further development for the deviated deep and hot wells common in the North Sea, where heat has affected the electrical pumps, and lowering the cable through angled holes has damaged the insulation.

A variant on this approach is to run the down-hole pump hydraulically. If the fluid used is crude oil then it may be discharged into the same stream as the reservoir fluid. The necessity to reinject cleaned-up oil must be balanced against the complexity of the additional pipework required for an effectively closed hydraulic system.

Rod Pumps

The fourth method uses a down-hole piston operated by sucker or pull rods, moved up and down by a rocking arm driven by a diesel or electric motor at surface. These 'Nodding Donkeys', in all shapes and sizes, are very common in the older oilfields of the world.

Figure 5 shows a typical pump with standing valve and travelling valve, both non-return valves designed to allow passage of fluid vertically upwards only. At the bottom of the rods the dynagraph card illustrates:

1 to 2: Rods stretching to pick up the load, i.e. column of fluid between piston and surface.
2 to 3: Piston is moving upwards; standing valve open.
3 to 4: Rods losing stretch and load transfers to standing valve which has closed.
4 to 1: Piston moving down; travelling valve open.

The principle is thus straightforward, but there are a large number of complications. The diagram shows what happens at the piston, not at the surface. As already noted the sucker rods themselves stretch, and unless the tubing string itself is firmly anchored this will also move up and down. The load on the prime mover thus varies in a complex fashion as the bottom of the system is out of phase with the top, and both static and dynamic effects come into play. It is a damped elastic system and resonance of the rod system must be avoided, otherwise the elastic vibrations due to the forced harmonics and those due to the natural frequency of the rods could reinforce each other to cause rod failure.

With the load on the prime mover varying throughout the cycle it is necessary to counterbalance it. A rotary counterbalance or eccentric on the crank or the compression of gas in a cylinder on the downstroke is commonly used.

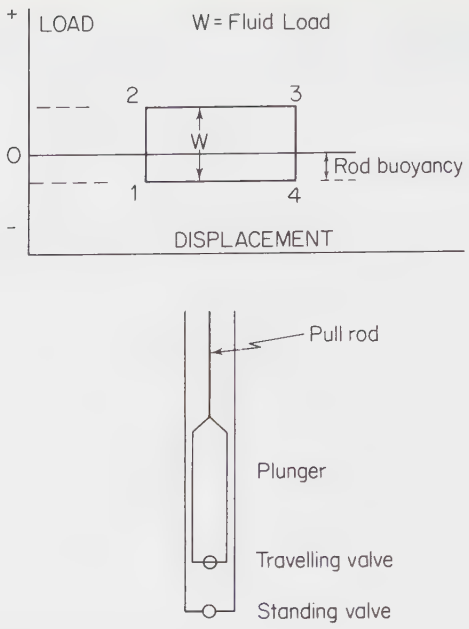

Fig. 5. Diagram of typical pump and dynagraph card.

Dynamometers can measure the stretch on the polished rod at surface and convert this into loads. The polished rod is the top of the pull-rod string and is packed off externally to ensure that the fluids do not leak past. The counterbalancing may be adjusted to smooth out the fluctuating loads, indicated by the dynamometers, to a large degree.

Dynamometers may also be used diagnostically to judge the performance of a pump and its associated equipment, using techniques analogous to a doctor employing an electrocardiograph to determine a patient's heart condition. Poor performance may be caused by leakage of fluid past the piston, or the standing or travelling valve; gas locking interfering with effective pumping; the tubing anchor slipping, and parted rods, to name some possible problems with characteristic dynagraph signatures.

This type of pumping is suitable for vertical relatively low-volume wells. It is extensively used in the older oilfield areas. With electric prime movers the units may be automated to run intermittently, perhaps only a few hours a week where the sole reservoir drive remaining is gravitational drainage into the well bore.

PRESSURE MAINTENANCE/SECONDARY RECOVERY

In the section on artificial lift methods for maintaining flow in a well as the reservoir pressure declines are briefly described. An increasingly common method of avoiding or delaying this drop in reservoir pressure is to replace the volume of oil removed with either gas or water. This is commonly referred to as secondary recovery, an expression originating from the days when the reservoir

pressure was allowed to drop virtually to zero and then gas or water was injected for a secondary sweep through the reservoir to flush out additional oil. Modern practice is to consider commencement of such injection much earlier in the life of the reservoir, and pressure maintenance is a better description of this process than secondary recovery.

To add further confusion to a loose terminology there is a group of techniques known as tertiary or enhanced oil recovery. These attempt to change the characteristics of the oil in the reservoir so as to aid its movement. Heat (reducing the oil's viscosity), miscible fluids (affecting viscosity and surface tension), polymers (changing the mobility ratio of the primary injected fluid or interfacial tension), *in situ* use of some of the oil as fuel by burning or otherwise consuming it (affecting viscosity and generating gas) are all used. While the last, either by injecting air and inducing combustion, or by using bacteria, is the most elegant solution to enhanced recovery, both are proving difficult in practice. Most of these techniques would also have the effect of maintaining reservoir pressure as a side-effect.

From the viewpoint of production the problems relate to the provision of the appropriate fluids, their injection into the well bore and, in some cases, their effect on the producing wells.

Water Injection

For water injection the proposed water will have been checked against the reservoir water to ensure that unacceptable precipitation of solid salts, due to the interaction of dissolved chemicals in the two waters, does not occur. Fresh water would avoid this possibility, but would be more likely to swell any interstitial clays within the reservoir. In many parts of the world fresh water is not available, and in these areas saline water obtained from water-bearing formations is used, or sea water.

It is necessary to ensure that the water will not plug the formation into which it is being pumped. Figure 6 shows an offshore schematic. Submerged electric pumps move sea water through down-flow sand filters, on through a de-oxygenating tower backed up by additional chemical injection to reduce the

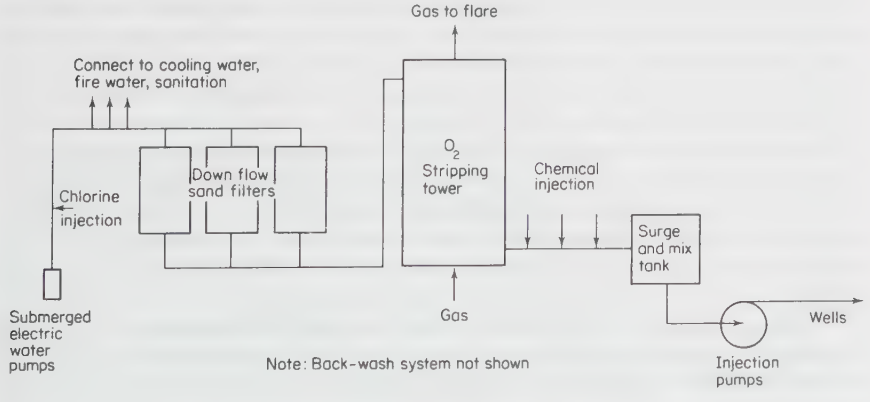

Fig. 6. Production platform flow diagram—injection water.

oxygen level further. A biocide will also be added and an anti-scaling agent. In this example centrifugal pumps are indicated for injection purposes. Because of the very high premium to reduce weight offshore some lightweight high-output filters are being developed. The full flow does not go through the filter, as in the illustration. These lightweight filters use membranes of sub-micron pore size which are arranged so that the filter surfaces are continually flushed with a flow of feed water. Some of the flow goes through the membrane, while some goes along it to reduce the rate of build-up of the fouling layer by providing a sweeping action. In tests 98 per cent of all particles 1 micron and above were removed from the water passing through the filter.

A potential problem with sea water picked up from under the platform is that it may have a significant oil content due to the oily water discharge from the platform's own production facilities. Cleaning accumulated oil from this new type of filter holds promise of being an advance on existing methods.

Onshore fresh or subsurface brackish or saline waters may be used. If handled in surface facilities similar treatment will be required to that discussed above before being pumped into the injection well by centrifugal or multi-piston reciprocating pumps.

In some situations a dump flood may be used. Here the injection well is perforated opposite a water-filled formation as well as opposite the oil-bearing reservoir, and the water transfers without coming to surface.

As reservoirs typically have a pressure that may be balanced by a column of sea water, approximately 0.46 psi/ft, water injection for pressure maintenance only requires to generate pressure to overcome well bore and formation resistance to inject water at the required rate.

Gas Injection

At the other end of the scale, while a column of gas at high pressure does have a weight, it is significantly lower than that of water. Thus, for any given reservoir pressure much higher pump pressures are required for gas injection than for water injection. For example, for a reservoir with 5000 psi bottom-hole pressure water injection at 2000 psi or gas injection at 6000 psi may be appropriate.

Compressing gas to these high pressures requires considerable engineering effort to achieve reliable operations. Difficulties have been experienced in the North Sea. However, after considerable engineering effort and modifications over a number of months gas injection plants in this area have cut their down-time to acceptable levels.

Centrifugal and reciprocating compressors are both used, and sometimes a combination, i.e. multi-stage centrifugals feeding a final reciprocating stage. Centrifugal compressors (and gas-turbine drives) have an advantage where weight, size, and vibration become matters of concern, i.e. offshore, but their thermodynamic efficiency is less than that of reciprocating pumps and diesel drives.

Injecting gas such as CO_2 and nitrogen requires similar plant to injecting hydrocarbon gas, but falls within the category of enhanced oil recovery or tertiary recovery, while gas (CH_4) injection is pressure maintenance or secondary recovery.

Thermal Methods

The application of heat to the oil reduces its viscosity and can make a dramatic difference to well productivity with high-viscosity crudes.

Steam drive has been used in the past for this purpose but is not common today. In this technique steam, at say 400 F, is injected into a well or wells and drives the warmed oil towards a pattern of producing wells. An example of a field in which this method was used is Kern River where 12° to 16.5° API oil, 4000 centipoise viscosity at the reservoir temperature of 90 F, was converted to steam drive after initial success with bottom-hole heaters had proved heat a successful mechanism.[2]

A more common method is steam soak in which steam is injected and then the well back-flowed. This is often referred to as the Huff and Puff method. This cycle may be repeated three or four times with diminishing returns on each successive cycle; a 7-day steam injection may be followed by enhanced oil production for up to 12 months. While the process may not be the most efficient in terms of ultimate oil recovery, it has tremendous attractions because of the rapid return on capital employed and the ability to estimate profitability after each cycle.

One of the problems found with this technique is the stress level generated within the well casing due to the marked changes in temperature between steam injection, 400°F and production, 100°F. One interesting method of solving this problem is to cement in only the bottom of the casing and use a petroleum-based gel for most of its length. The casing may then expand and contract in response to the changing temperatures experienced.

Down-hole steam generators are a fairly recent development. In one trial propane and air were piped to the bottom of the well and ignited in the combustion chamber by a spark plug. Water introduced into the combustion products is turned to steam and the combustion products (mainly CO_2 and N_2) and steam were injected into the reservoir. In another test a combination unit adapted to run on diesel fuel was used. To obviate the high temperatures resulting from continuous combustion another technique being evaluated is that of a pulsed burner. In this technique fuel and air are introduced into the combustion tube and ignited. The rapidly expanding combustion products pass out of the bottom of the tube where they turn water, passing down the annulus of well and combustion tube, into steam. After the combustion pulse further water passing the tube absorbs much of the heat before a further pulse and ignition are induced. This maintains a relatively low tube temperature. Again steam and the products of combustion will enter the reservoir.

A more elegant method of heating the oil is to burn some of it *in situ*. This will generate heat and gas at the interface rather than dissipating much of the heat during passage of steam from boiler to wellhead to formation, as occurs in most steam-drive processes. In some cases injecting air causes spontaneous ignition to occur, while in others thermal ignition is necessary. In the early stages of the project, while the fire front is close to the injection well, it is essential that the injection compressors are kept on stream. If they shut down burn back to the well bore may occur, with irreparable damage to the casing taking place.

In this process the production wells must be designed to handle very hot, corrosive products. Stainless steel liners and tubing may be employed to

TABLE I[6,7]

	Miscible processes				
	Nitrogen	High-pressure hydrocarbon gas	Enriched hydrocarbon gas	Carbon dioxide	Hydrocarbon solvents
Main mechanism	Removes sharp interface with oil				
Preferred oil	Medium to light gravity				
Beneficial conditions	High pressure diminishes in importance Possibility of significant gravity drainage				
Harmful conditions	Shallow reservoir, stratification, high mobility ratio, potential for asphaltene deposition				
Added recovery*	Up to 15%				
Total production costs†	15 32$/brl				

	'Chemical' processes			
	Polymers			
	Polyacrylamide	Polysaccharides	Surfactants	Caustic
Main mechanism	Improves mobility ratio		Reduces capillary trapping forces	Reduces interfacial tension by forming surfactants *in situ*
Preferred oil	10–100 cP viscosity		Low viscosity	Medium to heavy
Beneficial conditions	Under 80 °C§			
	Low salinity water in reservoir¶	Moderate salinity water in reservoir	Not too saline water: low reservoir rock clay content	Oil contains adequate amounts of organic acids

Harmful conditions	High water salinity; low permeability				
Added recovery*			Up to 15%		
Total production costs†			24–48$/brl		
			Thermal processes		
	Hot-water drive	Steam drive		Steam soak	*In situ* combustion
Main mechanism	Viscosity reduction				Viscosity reduction and miscibility arising from combustion products
Preferred oil			Heavy‡		
Beneficial conditions		Thick uniform reservoir rock; possibility of gravity drainage			Thick uniform sand; good permeability and high porosity
Harmful conditions	Deep reservoir				Presence of gas cap or water zone in operations area
Added recovery*			Up to 40%		
Total production costs†			15–30$/brl		

* Based on original oil in place.
† For conventional methods (primary and secondary recovery) 1.5–20$/bbl.
‡ For heavy oils (high viscosity) recovery by conventional methods is low.
§ Pressure (normally) and temperature increase with depth to the reservoir.
¶ The salinity of the water in the reservoir rock commonly increases with depth.

combat corrosion, and cooling water may be injected into the tubing–casing annulus to keep the bottom-hole temperature below 500°F. Surface cooling will then bring the produced oil, gas, and water down to more normal temperatures to allow normal separation techniques to be used.

Other Methods

The other methods of EOR (enhanced oil recovery) are generating a great deal of research. Possible polymers to augment water floods, increasing displacement efficiency by these 'thickening agents' reducing the mobility of water, are legion. Alkaline substances added to water should reduce the surface tension between the water and reservoir oil. Surfactant polymers also have the property of reducing the surface tension between oil and flood water. This should aid the development of an oil bank to be pushed along by following injected water to which a 'thickening' polymer will have been added.

Miscible processes include the injection of hydrocarbon gas or LPG (liquefied petroleum gas) which may dissolve in the trapped oil, reduce its viscosity, and again help the development of an oil bank which may be pushed along by subsequent injection of water. With the sales outlets often available these days for hydrocarbon gas and LPG, other gases are being investigated. Carbon dioxide, nitrogen, and flue gases are all being evaluated and a few field trials are in progress.

From a production point of view they are all variants on the theme of injecting a liquid or a gas, or a mixture of the two into the injection well.

To put EOR into perspective, however, it has been estimated that of the 600 000 bbl/day at present produced by these techniques more than 80 per cent is by thermal methods, with steam drive and steam soak providing the major part.

Table I gives a very generalized and concise summary of the salient features of the various techniques described under the label of EOR. Furthermore, it should be noted that EOR activities have to date been almost entirely in onshore fields and predominantly in North America; there have been restrictions on well spacing for most techniques and usually limits on the sizes of the projects. The challenge is whether processes can be developed for application globally to reservoirs of many different characteristics and also major size.

SURFACE SEPARATION

From the wellhead the oil passes through an appropriately sized pipeline to the train of separators. Onshore, with the wells spread all over the surface of the field and drilled vertically, these gathering lines may be some miles long to reach the separation plant. Offshore, where the wells are normally grouped on a platform and drilled directionally to spread out at reservoir depth, the pipework to the separation plant is relatively short.

The flow to the separator train in the early stages of the field's life will normally be oil and gas. Reservoir water may also be produced in increasing proportions over time. This water is saline and may be salt-saturated at reservoir temperatures, so that it is supersaturated at surface conditions.

Export crude from many Middle East reservoirs has a specification of less than 10 pounds of salt for 1000 bbl of oil. As the salinity of contained water may be over 200 000 ppm, this means that every effort is made by work-overs and control of well producing rates to maintain the wells essentially water-free. In parts of the world the water produced with the crude from some wells may range up to 90 per cent or higher, a condition which imposes practical restrictions on the rates at which the wells can be produced.

Where water is produced with the oil and gas turbulent passage through the pipework and fittings of the well bore, wellhead, and separator manifold before entering the separator often creates oil/water emulsions. These emulsions can be extremely tenacious and difficult to break. As the water content increases, however, some water will remain unemulsified.

Solid particles of reservoir material may also be entrained in the fluids, although the well completion will have been designed to prevent this, and if it occurs remedial work will be attempted using resins, etc. to stabilize the formation near the well bore.

The separation of gas, oil, and water is carried out by taking advantage of their different densities. Separators may be vertical, horizontal, or inclined. Internally a number of techniques are used to encourage separation of the fluids. As the production stream may be travelling at high speed centrifugal forces can be generated by appropriate entry and passage through the separator cylinder. Baffle plates, coalescing plates, mist pads, etc. are used to encourage oil to coalesce and fall while the gas rises. Including these items increases the weight of the separator, and Fig. 7 illustrates a recent lightweight

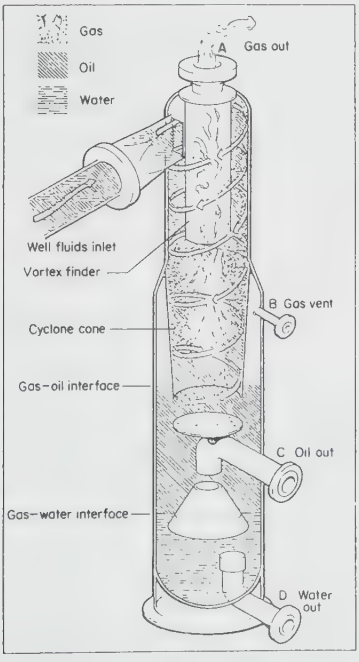

Fig. 7. Lightweight gas, oil, and water separator. (Illustration courtesy of Plenty Metrol.)

offshore design relying heavily on centrifugal effects to generate separation. At the entrance to the separator there is a vertical slot with an adjustable vane to allow velocity adjustment of the fluid film before it enters the cyclone tangentially. The oil film spirals down the walls of the cyclone, which is tapered to allow for energy loss during the oil's passage. Gas rises from the centre of the cyclone, and additional gas that is released after the oil film cascades out of the cyclone is released through vent B.

Figure 8 is a simple schematic showing that pressure within a separator is controlled via the gas outlet, while the gas/oil level is controlled at the oil outlet. Immediately downstream of this controller the pressure is falling towards that held in the next separator, and further gas will be coming out of solution.

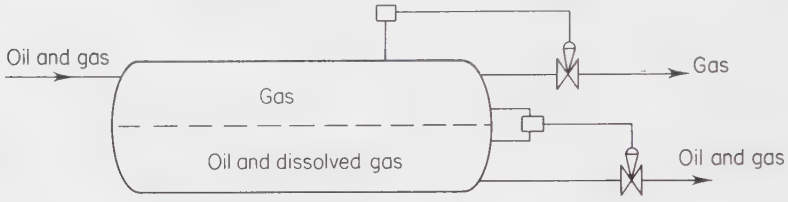

FIG. 8. Diagram of separator with pressure and gas/oil level controls.

When the well stream reaches the separator at a high pressure it is common to have more than one stage of separation. In general the higher the first stage of separation the higher will be the proportion of methane in the gas and the lower the proportion of the higher hydrocarbons. At subsequent, lower stage pressures, the proportion of methane in the gas drops while that of higher hydrocarbons rises. Calculating the equilibrium between gas and liquid phases in any actual case is complicated, because of the large number of components involved and variations in the equilibrium constants with pressure, temperature, and concentration.

In the Middle East, where gas used to be a source of local fuel, or was flared because of lack of any other outlet, four or five stages of separation were common to retain as much low-boiling hydrocarbons as possible in the crude oil.

With the development of LPG recovery from the separated gas streams and LPG export from many producing areas of the world the importance of retaining low-boiling hydrocarbons in the crude oil has somewhat decreased. However, the use of first-stage gas (the leanest in hydrocarbons heavier than methane) as fuel, gas lift, or injection gas, and a subsequent stage (or stages) with LPG recovery are not uncommon.

As an example of a separator train a 700 psi, 140 psi, 42 psi, and 14 psi (atmospheric tank) plant is visualized. This is typical of some found in the Middle East and the North Sea. Figure 4 illustrates the relationship between the oil and gas from the reservoir to the atmospheric tank, and it is assumed that the saturation pressure, the pressure at which gas first comes out of solution, is 2800 psi (200 bars).

4000 psi—Pressure at bottom of well—no free gas
2800 psi—Pressure somewhere in well bore—first gas being liberated
700 psi—Pressure in 1st stage separator; 75% of gas liberated
140 psi—Pressure in 2nd stage separator; 20% of gas liberated
42 psi —Pressure in 3rd stage separator; 3.5% of gas liberated
14 psi—Pressure in 4th stage separator; 1.5% of gas liberated

Converting these atmospheric pressure volumes into equivalent volumes at the relevant pressures we need to divide the percentage volume by the pressure of each stage expressed in bars:

1st stage: 75% divided by 50 = 1.5%
2nd stage: 20% divided by 10 = 2.0%
3rd stage: 3.5% divided by 3 = 1.2%
4th stage: 1.5% divided by 1 = 1.5%

showing that in volume terms each stage strips out approximately the same volume of gas when measured at separator pressure. Dimensionally this means that separators of similar sizes can be used.

Emulsion Breaking

Where emulsions have been formed it is necessary to break them after free water and gas have been removed. There is an enormous range of complex chemicals on the market to perform this task. The emulsion is often heated to speed the process.

Economically it is impossible to remove all the water. If the crude oil produced following emulsion breaking and water separation is unacceptably saline for the refinery, fresh water may be added during the clean-up process to 'wash-out' the salt. Whether this salt removal occurs at the production end or at the refinery depends on the area of the world involved; often crude oil de-salters form part of refinery equipment, since they can remove salt introduced during tanker transport.

Hydrogen Sulphide Removal

The presence of hydrogen sulphide in a reservoir flow stream is an added complication. For the fabrication of the pipework of well and separators it precludes the use of many high-grade steels, because embrittlement will occur. Thicker walls and lower-grade steels are used. For high-pressure wells with high hydrogen sulphide special materials are required for the wellhead. The disagreeable smell of rotten eggs, characteristic of hydrogen sulphide, is a well known product of the school chemistry laboratory. What must never be forgotten is that it extremely toxic. An atmosphere containing 1000 parts per million is instantaneously lethal. A danger is that exposure to H_2S quickly deadens the sense of smell. This may lead to a false sense of security, since disappearance of the smell after it has been first noticed, may be due to an increase rather than a reduction in concentration.

Precautions, therefore, are essential in any operation or location where the presence of hydrogen sulphide is possible whether expected (e.g. where sour

crude or gas occurs) or cannot be excluded (as in the first well entering an unknown formation). The precautions to be taken with H_2S are given in Chapter 9 of the IP Model Code of Safe Practice in the Petroleum Industry, Part 8 'Drilling and Production in Marine Areas'. These include the availability of breathing apparatus of the airline mask or other suitable positive pressure type for all personnel on such a site (canister respirators not being adequate or suitable). A hydrogen sulphide detector and alarm should also be installed on the platform and arranged to indicate the presence of H_2S in any enclosed space or where a leak is likely to occur.

Before gas can be sold it is necessary to remove the hydrogen sulphide. This is commonly done using an amine tower. The liquid amine percolating down through the rising gas absorbs the hydrogen sulphide. In a separate process the hydrogen sulphide is removed from the amine, which can then be recycled.

A recent development is the use of molecular sieves to trap the hydrogen sulphide, after which it can be recovered from the sieve in an ancillary regeneration process.

GAS TREATMENT AND DISPOSAL

How the gas is treated depends on its economic value.[5] Until the 1970s and because of lack of outlet much Middle East gas was flared untreated. With the rise in the market for natural gas liquids much is now treated to remove most liquefiable fractions. This is carried out by processing the rich (or 'wet') gas streams in either a compression/absorption or a refrigeration/absorption type plant, to produce 'lean' or 'dry' gas to meet pipeline specifications for hydrocarbon dew-point, etc., and the raw NGL (natural gas liquids). The raw NGL is then fractionated in a series of distillation columns, the first being a high-pressure de-ethanizer (to 'stabilize' the subsequent LPG product streams and return ethane gas to the gas stream), followed by a de-propanizer and then a de-butanizer column. From these two columns specification propane and butane LPG streams are obtained for sweetening to remove the H_2S or mercaptan sulphur before being dried and sent to storage, while the de-butanizer column stream (consisting of 'pentanes-plus' hydrocarbons or 'C_{5+}') is shipped as light gasoline for either petrochemical feedstock or as motor gasoline blend material.

These processes are normally carried out at a natural gas liquids refinery or terminal. The propane and butane LPG products are usually stored and transported in refrigerated form at near atmospheric pressure, for which they must be rigorously dried to remove all traces of water. In some installations an additional process step is used to recover and fractionate out the ethane, for use as steam cracking feedstock for ethylene manufacture. In the North Sea the situation is made more complex because storage and transport of both gas and NGL may be difficult or uneconomical. In the four-stage separation system discussed earlier the 700-psi gas would be almost entirely C_1 and C_2, with proportional increases in C_3 and C_4 as the pressure dropped in subsequent stages of separation.

In a sophisticated North Sea offshore system the gas from each stage would be compressed and NGL removed in a separator. The resultant 'dry' gas may still contain unacceptable quantities of hydrogen sulphide and water. As mentioned earlier the former is removed using an amine tower, either offshore

or onshore. While many chemicals may be used to suppress the formation of crystalline hydrates of water and hydrocarbons, North Sea practice is to remove water offshore. The moist gas is exposed to a counter-flow of glycol in a tower or contactor. The glycol absorbs the water and this is subsequently distilled out of the glycol which is re-used.

Some of the gas is used for fuel, the remainder may be piped ashore in a gas line, injected into the reservoir, or reintroduced to the oil and piped ashore dissolved in the oil.

The NGL can also be introduced into the oil pipeline or a gas pipeline and transported to shore. Its presence in a gas pipeline in large quantities will require the line to be swept clean, or pigged, to prevent adverse effects on the line's gas throughput, caused by liquid accumulating at low points in the pipeline.

WATER TREATMENT AND DISPOSAL

In the section on separation the presence of reservoir water and oil/water emulsions was mentioned. Disposal of this water can prove a problem.

Both onshore and offshore it may be possible to inject the oily production water into a disposal well. However, in many cases it is treated to reach an oil content acceptable to the authorities and discharged at surface.

The characteristics and quantities of this water vary considerably, both from field to field, and in any one field from time to time, often in near-random fashion. It may contain suspended solids such as clays, corrosion by-products and heavy hydrocarbon complexes, such as tar or wax. The buoyancy of these solids will be affected by the amounts of oil and gas adhering to them.

The use of demulsifiers, biocides, corrosion inhibitors, and other chemicals in the production process and secondary and tertiary recovery methods all can affect the characteristics of the water. Some produced water contains significant quantities of oil droplets smaller than 25 microns, while some components of crude oil may be significantly soluble in the water. These soluble components are usually also the more volatile and better biodegradable components.

The simplest method of gravity separation is a settling tank, sump, or caisson. Offshore, where long residence time would be unacceptable, plate interceptors are often used to reduce the effective depth of the fluid column and to aid separation. These systems of densely packed plates, like gas/oil separators, come in a variety of styles. Corrugated, parallel, and tilted plate separators are all in use. They appear to be effective on droplets of diameter above 60–150 microns.

A method of accelerating the process is gas or air flotation, where separation is stimulated by the small bubbles adhering to the oil droplets and speeding their ascent. Other methods used onshore include coalescers, filters, electrostatic precipitators, membrane processes, and biological treatment, but none are common offshore.

SAFETY PRECAUTIONS

Safety is an essential precept in the operations of drilling and producing oil and gas, and basic guidance may be found in the IP Model Codes of Safe Practice in

the Petroleum Industry, Part 4 (Drilling and Production Safety Code for land operation), and Part 8 (Drilling and Production in Marine Areas Safety Code), and in the various codes and standards of the American Petroleum Institute. The detailed UK Department of Energy Notes for Guidance on Design and Construction of Offshore Installations (HM Stationery Office) are also an essential requirement for those engaged in operations in the North Sea, as also is the British Standard BS 6235, 1982, Fixed Offshore Structures (BSI, 2 Park Street, London W1A 2BS).

CONCLUSION

The above discussion has attempted to describe the production process from reservoir to the separation of the hydrocarbons into saleable primary products.

The separation of wells into flowing and artifical-lift indicated that most wells will go from the former to the latter during the course of their lives. Similarly, the probability of increased volumes of water over time has been mentioned. The gas/oil ratio and the quality of the gas may also change with time.

Unlike many other process facilities, therefore, oilfield production and equipment must be designed with the flexibility to adapt to changes in reservoir pressure and fluid produced over the life of the field.

At the beginning of the chapter the role of the reservoir engineer in establishing the development scenario was emphasized. His role continues throughout the life of the field to update predictions of its future behaviour. Using these predictions the production engineer will make modifications to his systems to maintain production of the field as long as it is economically possible. Estimating the cut-off point, involving assumptions about future costs and product prices and taxes, is outside the scope of this chapter, but is critical for the initial development of marginal oilfields, and for many plant modification decisions in developed fields.

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7

Transport by Pipeline

By W. M. C. JONES and K. F. PADDOCK

THE modern steel butt-welded pipeline has proved to be one of the most reliable and economic means of transporting oil and oil products. It differs from other forms of transport in that it provides a continuous process and not a batch process, as with ships or road or rail vehicles. The pipeline is, therefore, subject to different economic factors. With the various batch methods of transport the total quantity to be transported has little effect on unit costs once the quantity is sufficient to justify the use of the largest practical carrier unit, but as a rule, unit costs become less as the distance involved increases. Pipeline unit costs, on the other hand, fall with increasing quantities, and distance has very little effect. Figures 1 and 2, taken from M. E. Hubbard's paper on 'The Comparative Costs

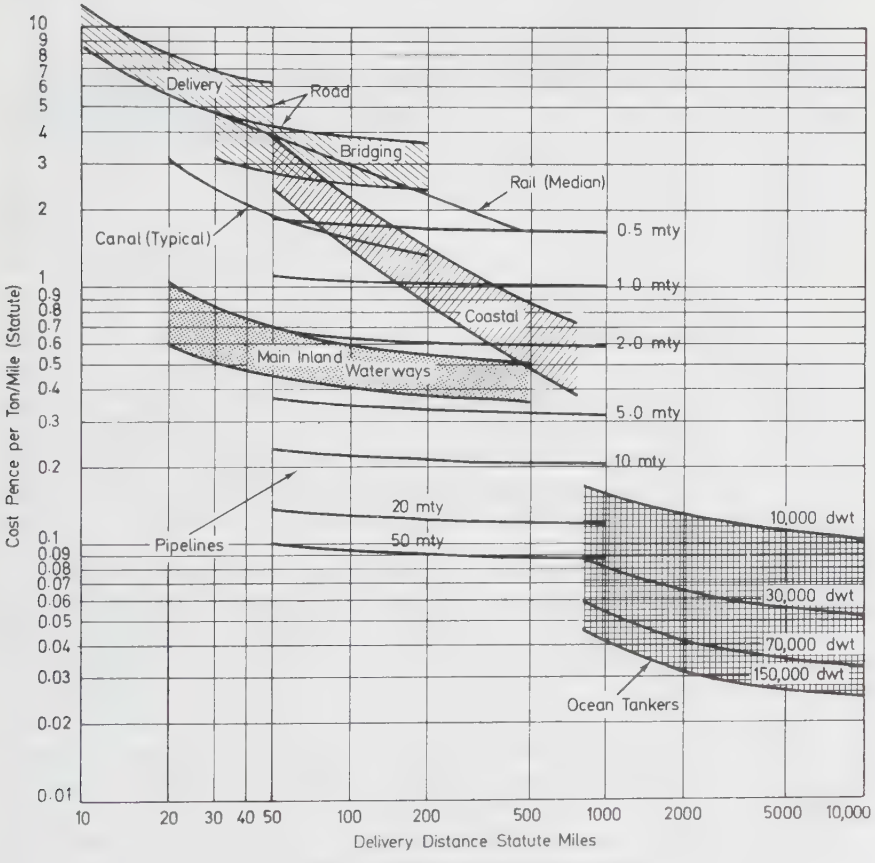

FIG. 1. Costs of transport relative to distance.

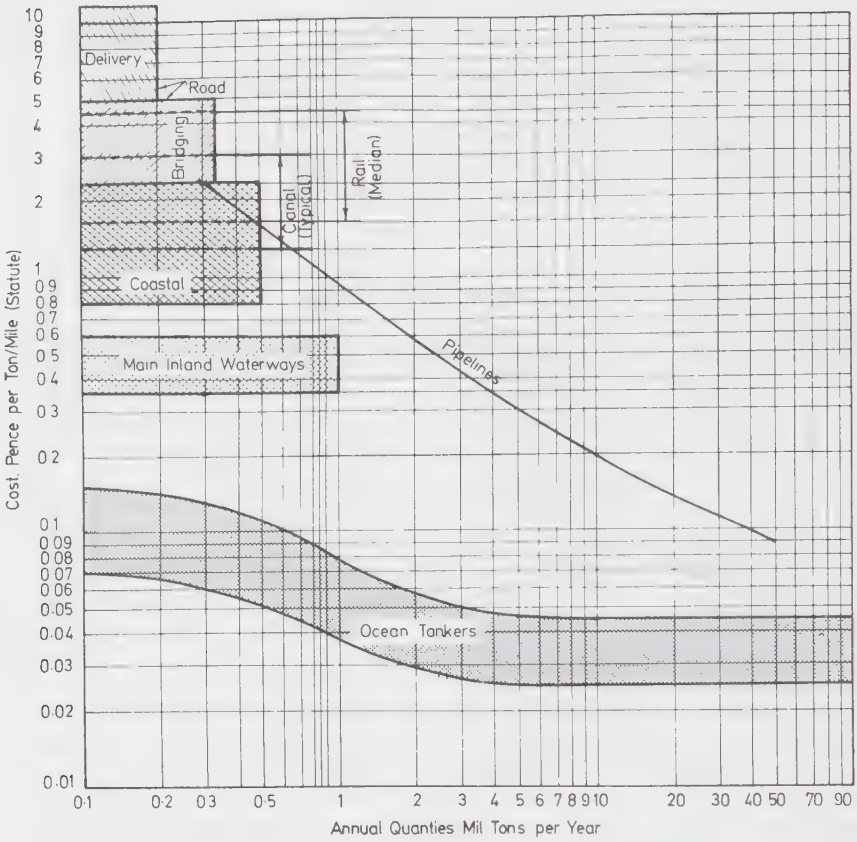

FIG. 2. Costs of transport relative to annual quantities.

of Oil Transport to and within Europe',[1] show this comparison. (The costs quoted on Figs 1, 2, and 3 preceded decimilization. Also, by 1982 inflation had reduced the Pound Sterling to about one-fifth of its 1967 value.)

To obtain the full benefit of the economy offered by any pipeline it is necessary to operate at its optimum capacity; this is a definite figure for each particular pipeline and is indicated by the minima of the curves shown in Fig. 3. Note, however, that this does not give the minimum unit cost for that particular quantity. For example, a 12-inch pipeline shows a minimum unit cost at a throughput of $3\frac{1}{2}$ million tons/year. But at this throughput a 16-inch pipeline shows a significantly lower unit transportation cost. From Fig. 3 it will be seen that there are definite ranges of throughput for which one pipeline diameter gives the lowest unit operating costs. Since there is an ever-changing demand for petroleum products, the quantity of oil to be conveyed by a pipeline is not a constant figure, and it is necessary, therefore, to assess the range of throughputs over a given time and to base the selection of pipeline diameter on this range.

Figure 4 shows how unit costs might vary during the lifetime of a pipeline when the ultimate throughput is double the initial throughput. This assumes that the

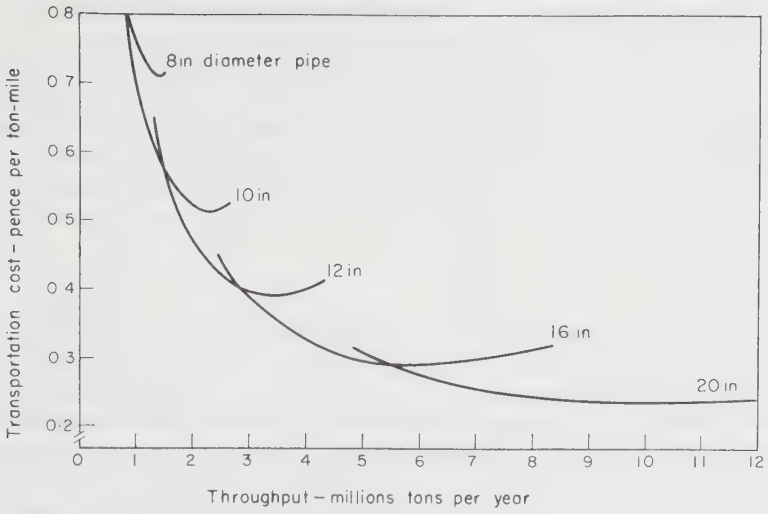

Fig. 3. Pipeline diameter and transportation cost related to throughput.

ultimate potential is attained by doubling the number of pumping stations. When first commissioned, with half the ultimate number of pumping stations, the pipeline will have an initial potential of about 70 per cent of the ultimate potential.

From point A to point B the throughput increases from 50 to 70 per cent of the ultimate potential (i.e. approx 70 to 100 per cent of the initial potential) with unit costs falling from 122 to 104 per cent. After the installation of the additional pumping equipment, unit costs will rise from point B to point C to

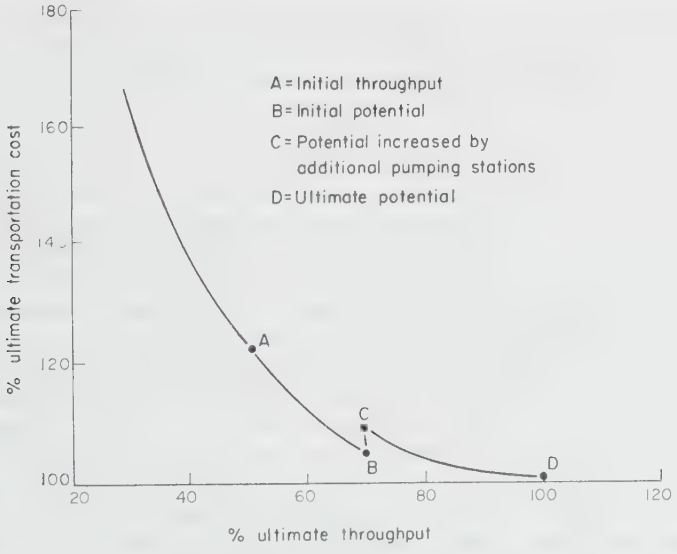

Fig. 4. Transportation cost related to utilization.

about 108 per cent at the 70 per cent utilization factor, but will fall to 100 per cent at point D as the throughput reaches the ultimate potential.

Transportation costs vary with the particular pipeline duty, being least when a single low-viscosity fluid is handled. Multi-product pipelines are usually more complex, feeding a number of installations, perhaps having branch lines, and are therefore more expensive to operate. Insulated pipelines for handling hot fuel oils are still more expensive to operate because of fixed charges on a higher capital cost and the increased power required to handle viscous oils.

I. GENERAL CONSIDERATIONS AND LAND PIPELINES

Crude Oil Pipelines

Crude oil pipelines may convey the production from one oilfield to a refinery, different grades of crude from different sources, or crudes for different owners to different refineries along the pipeline route. Where different grades of crude are involved the switching of flow from one storage to another is often based on quantity measurements rather than on any change in the crude characteristics, since the amounts of mixed crudes which occur at interfaces do not, in general, significantly affect subsequent refining processes. Where, however, a stricter control on crude quality is required it is necessary to measure some property, such as specific gravity, at a particular point, so that switching can be timed to coincide with a change in the property measured. Some crudes with a high pour point are pumped into pipelines at elevated temperatures of 50 to 60 °C, and such pipelines are often laid at somewhat greater depths than normal.

Products Pipelines

These are generally designed to convey a range of products from naphtha to gas oil, the so-called white or clean oils. The products to be handled are despatched in a definite sequence, e.g. naphtha, gasoline, kerosine, gas oil, kerosine, gasoline, naphtha. The rate of flow in multi-product pipelines has a direct bearing on the extent of intermingling of successive products. In the first place the velocity must be such that the Reynolds Number is above the 2000 to 3000 range below which flow is laminar. Laminar flow would result in complete mixing of products. It has been established[2] that there is a further critical value of Reynolds Number at which the rate of intermingling shows a sharp decrease. This critical value varies with pipe diameter as shown in Table 1.

The switching into appropriate tankage of the different products as they arrive at their destination is based on measurements made by an interface detector, which usually measures the specific gravity of the product flowing past it. Other properties, such as dielectric constant or viscosity have also been used. Spheres, made of thick synthetic rubber and capable of being inflated with water to a diameter slightly larger than the bore of the pipeline, are sometimes used to reduce the amount of intermingling at the interface between two products. Spheres are introduced into the pipeline through special sphere launchers at the origin of the pipeline as the switch from one product to another is made.

TABLE I
Critical Reynolds Numbers

d inches	Critical value of Reynolds Number
4	22 000
6	29 000
8	34 000
10	40 000
12	46 000
14	72 000

At installations fed by a multi-product pipeline where interfaces are received it is necessary to provide separate interface holding tanks. These hold the interfacial mixture of the two products until it can be disposed of, usually by blending into a large volume of a compatible product in a proportion that will not put that product off specification.

Insulated Pipelines

Pipelines designed to convey fuel oils at temperatures considerably higher than ambient require to be thermally insulated so that the heat lost during transit can be kept to a minimum. The insulating material currently in common use is foamed polyurethane. This material may be obtained in pre-formed sections, applied directly to the pipe or applied to an annulus between the pipe and an outer polyethylene sheath.

The fuel oil is usually heated to about 95 °C before being delivered to the pipeline, and insulated pipelines have hitherto been confined to comparatively short distances of less than 30 miles, or greater if en-route re-heating stations are provided. An insulated pipeline runs from Fawley to West London, a distance of 64 miles. This pipeline was designed to handle between $1\frac{1}{2}$ and 2 million tons/year without intermediate pumping or heating stations.

Gas Pipelines

Pipelines used for the transmission, as distinct from the distribution, of natural gas are very similar to oil pipelines although there are some differences in route selection and in design. Because natural gas is not likely to cause pollution of water supplies less account may be taken of the presence of exposed aquifers or other vulnerable water areas along the route. On the other hand, a failure of a high-pressure gas pipeline could lead to the sudden release of a large quantity of stored energy with catastrophic results. Greater care has therefore to be taken in avoiding built-up areas, or if this is not possible in providing other safeguards.

Design

The first problem in the design of a pipeline is to decide the range of throughputs for which the pipeline is to cater and to select an appropriate

diameter for that range. At this stage one of the many published charts showing pressure/throughput relationships may be used to give a first approximation of the diameters and associated pressures to cater for both the initial and ultimate throughputs, bearing in mind that 1000 to 1200 psi is a normal pipeline operating pressure. (1440 psi is the limiting working pressure for Series 600 fittings and this, no doubt, has affected the selection of normal pipeline operating pressures.) The first approximation will, as often as not, lead to a choice of solutions, e.g. for a pipeline about 100 to 120 miles long to carry, say, 2 to 5 million tons/year the possible solutions may be (1) a 12-inch dia pipeline with one pump station initially, with a midway booster station added later and then two further booster stations at the quarter points added to give the ultimate throughput: (2) a 14-inch dia pipeline with one pump station initially and a midway booster station added to give the ultimate throughput; or (3) a 16-inch dia pipeline with a single pump station that is capable of satisfying the ultimate throughput. In the first case the minimum amount of capital is spent to bring the pipeline into operation and further capital expenditure is incurred as increased capacity is required. This results in a fairly high utilization of the capital assets at any particular time. In the third case, the pipeline will be under-utilized for many years, and thus a certain amount of capital will have been spent unnecessarily early. The merits of the different solutions must be calculated from a financial aspect before a final choice is made.

Once the diameter of the pipeline has been established, more accurate calculations should be made to determine working pressures, surge pressures and hence design pressures. Suitable formulae are given in references 3 and 4 for oil and gas pipelines and in 5 for heated oil pipelines.

Pipe Selection

Pipes normally used for oil and gas pipelines are those complying with API Standards 5L or 5LX. Standard 5L includes two grades of steel, Grades A and B and Standard 5LX covers six grades: X42, X46, X52, X56, X60, and X65, the number representing in thousands of pounds per square inch the minimum specified yield strength. Pipe thicknesses are determined from the formula

$$t = \frac{PD}{2SF}$$

where P = maximum operating pressure,
D = external diameter of the pipe,
S = specified minimum yield strength,
F = a design factor,
t = design thickness of the pipe.

F is usually taken as 0.72 for most applications. For gas pipelines in built-up areas lower values of F are often used because the consequences of a failure are so much more disastrous. The adoption of lower design factors (0.6, 0.5, and 0.4 are sometimes used according to circumstances) results in the selection of a thicker pipe, but this does not necessarily mean that any greater safety has been achieved. A study of gas pipeline failures[6] over a considerable period shows that two causes account for the majority of failures, these being external damage

caused by other excavation operations, and external corrosion. The increase in thickness given by reducing the design factor down to 0.4 may not give adequate protection from failure from these two causes. Failure due to external corrosion is best prevented by the proper application of protective coatings and cathodic protection, rather than by the adoption of lower design factors. Careful siting, liberal use of pipeline markers, or some positive form of protection such as a concrete slab, may be more effective than the use of lower design factors in preventing failures due to external damage. Reference may be made to publication No. 674 of The Institution of Gas Engineers for considerations of design factors and safety precautions relevant to high-pressure gas pipelines.[7]

Profiles and Hydraulic Gradients

Except in mountainous country the profile of the pipeline route has very little effect on the overall pumping problem, but does decide the location of intermediate pumping stations. Figure 5 shows the hydraulic gradients for a one-, two-, or four-pumping station system on a 300-mile pipeline along a route

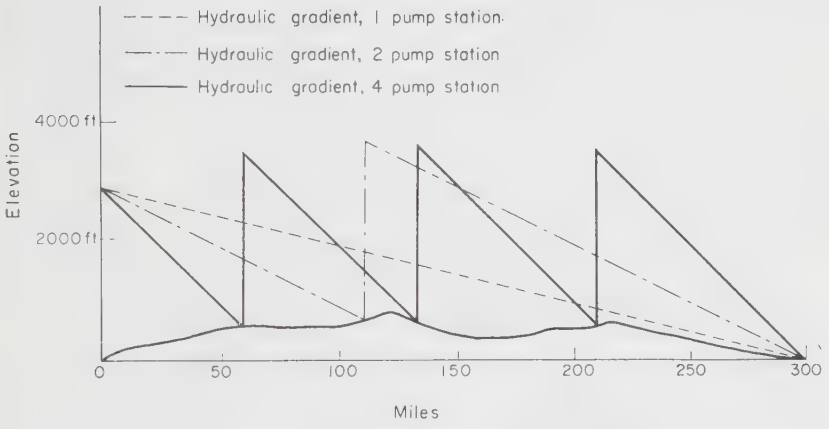

Fig. 5. Hydraulic gradients for pipelines. ---- Hydraulic gradient, 1-pump station; —.— Hydraulic gradient, 2-pump station; —— Hydraulic gradient, 4-pump station.

where the differences in elevation are small compared to the pumping head. It will be seen that for a two-pump station system, the second station should be sited at mile 115. If, however, the system is eventually to have four stations, then the 'mid-point' station should be sited at mile 135, as this gives a more even distribution of pumping duties when the third and fourth stations are added.

Complications arise when there is high ground near the end of any one pumping stretch. Figure 6 shows a profile of such a section. A pressure of P_1 is required to overcome the static head represented by point B before any flow can be established. For pressures between P_1 and P_2 the hydraulic gradient from the pumping station to point B is flatter than the natural gravity gradient

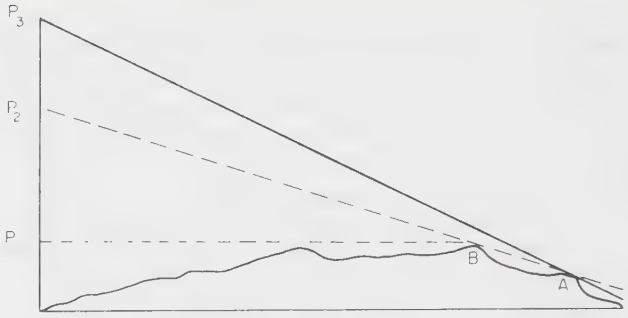

FIG. 6. Profile of pipeline route with high ground near end.

between points B and A. For pressures between P_2 and P_3, point A becomes the controlling point.

Unless back pressure is maintained at the receiving end so that pressures at points A and B are always positive, i.e. the hydraulic gradient is kept above the route profile, vapour spaces will form at these points and the pipeline will no longer run full. Problems then arise in comparing quantities despatched and quantities received owing to the wide variation in pipeline contents at different throughputs.

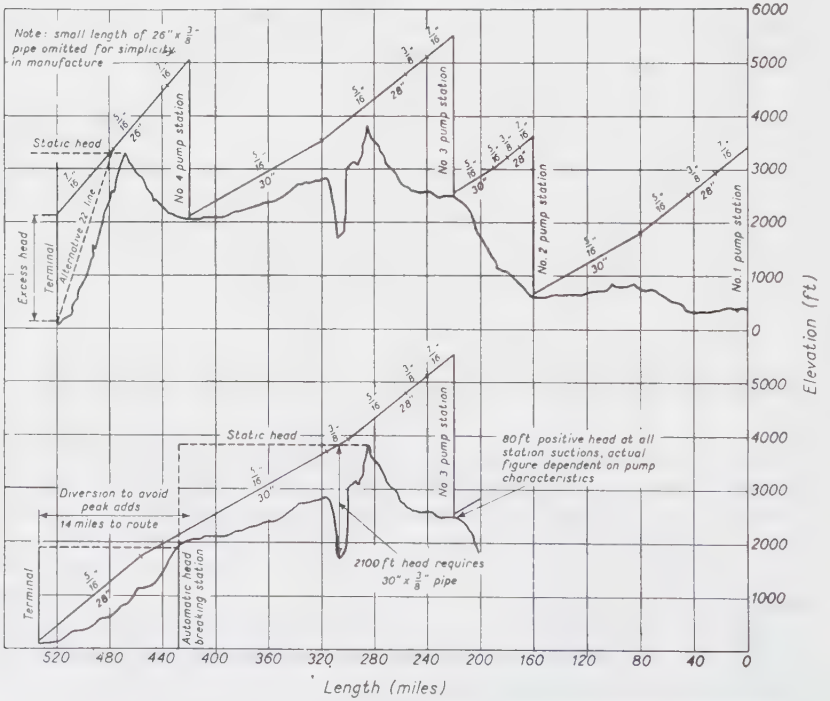
Note: small length of 26" x 3/8" pipe omitted for simplicity in manufacture
Static head
Excess head
Terminal
Alternative 22" line
No 4 pump station
No 3 pump station
No. 2 pump station
No. 1 pump station
Elevation (ft.)
Static head
Diversion to avoid peak adds
14 miles to route
Terminal
Automatic head breaking station
2100 ft. head requires 30" x 3/8" pipe
80 ft positive head at all station suctions, actual figure dependent on pump characteristics
Length (miles)

FIG. 7. Profile and hydraulic gradients of pipeline where elevation differences are comparable to pumping heads.

In mountainous countries, where differences in elevation are comparable to pumping heads, the siting of intermediate pumping stations becomes much more complicated. There is also a need for pressure control and relief stations to ensure that on downhill sections or in deep valleys, pressure does not exceed the permissible operating pressure of the pipeline. An example of this type of profile is given in Fig. 7.

Pumping Stations

The choice of pumping equipment will depend largely on the location of the pumping station. If adequate electrical power is available, then electric motor driven centrifugal pumps are the normal choice. Diesel engines or gas turbines, both of which may draw their fuel supplies from the pipeline, are the usual alternatives when electric power is not available. Electrically-driven pumps lend themselves readily to outdoor installation, and it is no longer considered necessary to provide a building to house such equipment.

The choice of pumps will depend on the pressure/throughput relationship of the pipeline to be served. Figure 8 shows typical pressure/throughput curves for a pipeline and for centrifugal pumps operating singly or in series. The throughput obtained with one pump at normal speed will be that given by the intersection of the single pump curve with the pipeline curve, namely about 1500 UK gal/min at 540 psi. For lower throughputs the pump speed may be reduced, giving, in effect, new pump curves represented by the dotted lines. If a constant speed pump is used, then a pressure control valve will be required on

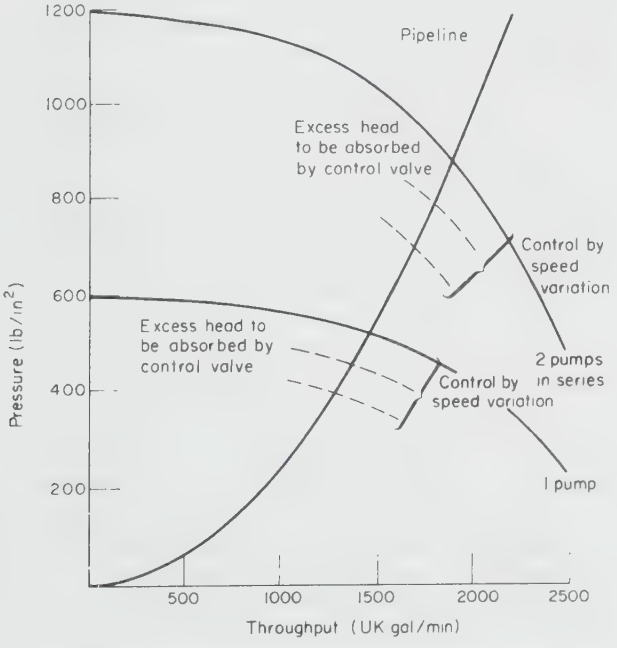

Fig. 8. Pressure/throughput curves; pipeline and pumps.

the discharge side of the pump to absorb the differences in pressure between that generated by the pump and that required by the pipeline. Similar controls will be needed for two pumps in series for throughputs between 1500 and 1900 UK gal/min.

Legislation, Survey and Land

The construction of a pipeline invariably involves encroachment on the rights of individuals owning or occupying land along the route and is therefore governed by legislation in most countries. The object of the legislation is usually threefold: to ensure that the rights of individuals are properly safeguarded, to make it possible to acquire rights compulsorily if this can be shown to be in the public interest, and to ensure that pipelines are built and operated in a safe manner.

An ideal pipeline would follow a straight line between its two ends. In practice, however, there will be many factors which tend to make a pipeline route a series of straight lines between adjacent control points, the control points being given by such factors as the best place to cross a river, avoidance of built-up areas, the use of passes in hilly country, the presence of vulnerable water areas, and perhaps even international boundaries. After selection of a preliminary route from existing maps a study of aerial photographs of the route, if available, will save much time in later survey work. The route should then be accurately surveyed and details of soil or rock conditions, land ownership and such other information as may be required by the legislation of the country concerned should be collected.

In negotiating for rights it should be appreciated that temporary occupation of a working strip will be required for construction as well as for the permanent easement for the pipeline. The width of the latter will to some extent depend on the relevant legislation, and is generally of the order of 20 ft plus the diameter of the pipe. The width of the working strip, will depend on the type of construction equipment to be used and the depth of the ditch to be dug. In general, 40 ft should be considered as a minimum width for equipment to lay up to, say, 12-inch diameter pipe in a 4-ft deep ditch. The restriction of the working width below the minimum dictated by the size of the equipment and the ditch is a false economy to both pipeline promoter and land owner, since it may lead to more expensive working in cramped quarters with consequent greater damage to the land.

Construction

Modern construction methods entail the deployment of a considerable amount of heavy equipment along the route of the pipeline. Careful study and planning are required to ensure that the equipment is properly balanced, that it moves forward at a steady rate and that different sections keep to the same rate of progress. The order of operations will vary with the type of country traversed and with weather conditions. While construction work is going on it is important to maintain a good relationship with landowners and occupiers along the route, and to ensure that the temporary occupation of the land does not go beyond the terms under which the necessary rights and consents have

been granted. Codes of practice published by The Institute of Petroleum and the British Standards Institution give good guidance on the design and construction of pipelines for the petroleum industry.[8,9] A very brief description of modern construction methods is given below.

Clearing and grading

These consist of clearing away all debris, removing scrub and hedges, setting up temporary fencing where required, and generally making the right-of-way suitable for the subsequent passage of construction equipment.

Stringing

This consists of distributing pipes in a single line along the route more or less adjacent to the position each will finally occupy. Wheeled vehicles are certainly best for the road part of the journey, but track-laying vehicles are preferable for travelling along the right-of-way, more particularly if wet weather is likely to be encountered.

Bending

Changes of direction may be made by using a bending machine to put a permanent set in the pipe. This machine is a comparatively heavy piece of equipment to be towed along the right-of-way to each spot where it is required, and the use of gentle curves, say, of a radius of 1000 times the pipe diameter, will allow advantage to be taken of the natural flexibility of a steel pipeline and so obviate a considerable number of set bends. The natural flexibility is often used to cater for changes in slope (vertical curves), but there is sometimes an unjustified prejudice against using it in a horizontal plane.

Ditching

Pipe ditches are usually dug to a depth sufficient to provide a cover of 3 ft and a width of 12 inches greater than the pipe diameter. Considerable thought should be given to the timing of ditching operations in relation to other pipe-laying operations. In good firm soil, in a dry climate, a ditch will probably stand for a considerable time, and it may with advantage be dug before the welding of the pipe. In poor soils, or in wet weather, there is a danger of the ditch sides collapsing, and the ditch should not be dug until the welded pipeline is ready to be placed and the ditch backfilled.

Welding

The field welding of pipes is governed by such standards as API Standard 1104, or British Standard 4515.[10,11] These standards set out the establishment of a welding procedure, requirements for testing welders in that procedure and standards of acceptance for field welds. Welds may be inspected visually whilst they are being made or by non-destructive methods after they have been made. All welds should be inspected by one means or another, and this usually implies

visual or ultrasonic examination of every weld. In addition, examination by radiographic methods should be applied to at least 10 per cent of the welds along the run of the pipeline. This percentage should be increased to not less than 50 per cent where the pipeline crosses a vulnerable water area (e.g. an exposed aquifer), and to 100 per cent for welds made under roads, railways, canals, rivers, or in other locations where subsequent access would be difficult. All tie-in welds (i.e. welds connecting together two previously welded sections of pipeline) should be radiographically examined (Figs 9 and 10).

Coating and wrapping

Steel is subject to quite rapid corrosion when buried in the earth, and the steel pipeline has become a practical proposition only because it can be protected against external corrosion. The first line of defence in this protection is a high quality coating applied to the pipeline with the object of electrically insulating the pipe steel from the surrounding earth. Coating materials may be hot-applied enamels, either coal tar or bitumen based, reinforced with a glass-fibre fabric and protected externally by a final wrap of enamel-impregnated glass fibre or by a strong paper wrap. Other materials such as cold-applied enamels and proprietary tapes may also be used. Coatings may be applied to

FIG. 9. Welding sections of the pipeline together is a skilled job. Some of the welding is done manually and some by an automatic process. However, the standard of welding is uniformly high and each weld is carefully inspected to ensure the integrity of the pipeline. (Photograph courtesy of British Gas Corporation.)

individual pipes at the pipe mill, at a coating yard on the site of the pipeline, or by line-travelling machines on to a completed section of the pipeline. The choice will depend much upon the amount of handling which the pipes will have to sustain between mill and final site and upon the suitability of the alignment and climate for the application of coating by line-travelling machines. All completed coatings should be checked by using a suitable holiday detector.

Lowering and backfilling

When soil and other conditions have allowed the ditch to be excavated previously and line-travelling coating machines are used, the coated pipeline

FIG. 10. When a pipeline is laid through agricultural land, the limited width of the 'easement' is soon restored and back in farming use. (Photograph courtesy of British Gas Corporation.)

may be lowered directly from the machine into the ditch. In other cases completed sections are laid on timber skids, with straw- or plastic-filled bags to protect the coating, and then picked up and lowered into the ditch by side-boom tractors (Fig. 11).

Excavated earth should be returned as backfill as soon as possible after the pipeline has been lowered, maintaining where necessary the original soil sequence.

FIG. 11. Once the pipeline is strung out along the route and welded into a continuous line, it is lowered into a pre-cut trench using large machines called sidebooms. (Photograph courtesy of British Gas Corporation.)

Clean-up and reinstatement

After all backfilling has been completed and all damaged land drains re-established, the surface should be cleared of all debris and reinstated as near its original condition as possible.

Cathodic protection

The use of a high-quality coating as the first line of defence against external corrosion has already been mentioned. Cathodic protection is used to back-up this defence by maintaining the pipeline at a minimum negative potential with respect to the surrounding earth. The impressed current system is more usual on long pipelines, whilst sacrificial anodes are normally used on short lines or to give additional protection in congested areas. Current consumption should be carefully recorded during the operating life of the pipeline as this gives an indication of the degree of deterioration of the coating. Pipe-to-soil potential surveys should be carried out at approximately six-monthly intervals so that sections not being properly protected may be located. Such sections may then be subject to remedial action such as repairs to damaged coatings, recoating, or the provision of additional cathodic protection. In this way external corrosion may be halted before it has reached the stage where leakage from the pipeline may occur.

Testing

Hydrostatic testing of completed pipelines has been a regular procedure for many years, the test being used to demonstrate that the pipeline is free from leaks and can withstand pressures well above the expected maximum operating pressure. Codes of Practice invariably specify a minimum pressure for hydrostatic tests, but give little or no guidance regarding a maximum. Today there is a growing tendency to use the hydrostatic test to determine the actual strength of the pipeline 'as built', by testing to a pressure which produces yielding of the pipeline. In order to detect the first indication of yielding, a pressure/volume plot is made whilst the test is in progress, and the use of suitably expanded pressure scales allows small changes in the pressure/volume relationship to be readily detected.

Figure 12 shows a typical pressure/volume plot for a 10-mile section of 18 × 0.312 inch pipeline in 5LX 52 pipe. Initial deviation occurs at 1800 psi, the pressure equivalent to 100 per cent specified minimum yield strength calculated on nominal thickness. This test was carried on up to 1980 psi or 110 per cent of specified minimum yield strength. Experience on testing to pressures above those representing 90 per cent of specified minimum yield strength shows that, as expected, there are more failures during testing, and consequently more defects are removed. Many of the defects removed are of a nature that would probably have led in time to a failure when the pipeline was in service. Tests carried out with an internal gauging pig capable of measuring changes in diameter as small as 0.03 inches in 30 inch pipeline show that over 99 per cent of the total length yields less than $\frac{1}{4}$ per cent and less than 0.1 per cent yields between $\frac{1}{2}$ and $\frac{3}{4}$ per cent. It is claimed[12] that by subjecting a pipeline to yield

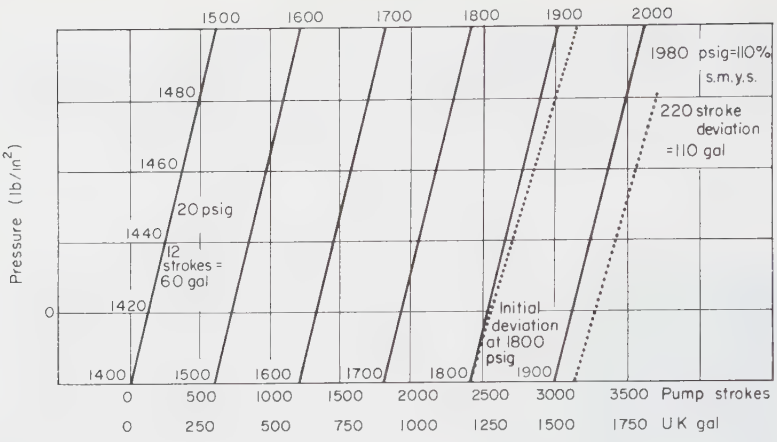

FIG. 12. Pressure/volume plot for 10 mile section of 18 × 0.312 inches API 5LX 52 pipeline.

testing certain secondary stresses which arise during construction are relieved, and that any defects remaining in the pipeline are so small that they can never become critical under operating conditions.

Whatever the test pressure may be, the petroleum pipeline is expected on its final test to hold that pressure for a period of not less than 24 hr, during which time there should be no drop in pressure that cannot be fully accounted for by temperature changes.

Control

One of the most important developments in pipeline operations is the use of telemetry and telecontrol. Communication circuits along the entire length of the pipeline system, with connections at all relevant points, allow the pipeline to be controlled from a single point. Basically three types of messages are carried by the communication system: (1) measurements of parameters such as pressure, flow volume, temperature, (2) indication of state such as valve open or closed, motors running and (3) control signals to open or close valves, start or stop motors. (1) and (2) provide the controller with information which shows whether the pipeline is operating in the manner desired at any particular time, whilst (3) allows the controller to alter operating conditions to suit pre-arranged pumping programmes. The ability to control valves and pumping units remotely has led to the unattended pump station where additional sensors are installed to indicate certain mechanical functions, e.g. temperatures of pump bearings, pump casing and motor windings, electrical overload, vibration, etc. When the measurements of these functions go beyond predetermined values an alarm signal is transmitted via the telemetry system to the central control, from where a standby pumping unit, if available, may be started up and the offending unit shut down, if the latter has not already been accomplished by local automatic circuits.

The translation of information received via telemetry into signals sent out from the control centre to control the operation of a pipeline is an area in which

computers can be used, but in general, decision making is still left to a pipeline controller. Certain automatic sequences can, however, be readily incorporated in a remote control system, so that a single command from a control centre will set in motion a chain of events automatically sequenced by the local equipment. Such sequences would cover, say, starting up motors and pumps, or running meter provers. A fixed programme computer may be used to determine meter factors needed to compensate for changes in temperature, viscosity or bulk modulus of the products being handled. A computer may also be used to make comparisons between meter readings at all input and outlet points of a pipeline system and so give an indication of the integrity of the system. Some discrepancies between total input and output will occur owing to different accuracies of different parts of the metering system and slightly varying contents of the pipeline as temperatures and pressure vary. Nevertheless. monitoring of this nature can be an extremely useful tool in detecting, or confirming the absence of, leakages.

The communication circuits may be carried by radio links, by a cable or overhead line running along the pipeline route or by circuits rented from a national telecommunication system.

II. SUBMARINE PIPELINES

Consideration of submarine pipelines differs from that of land pipelines in as much that: (a) the stresses induced during laying are considerably more in the submarine context; (b) that in the majority of cases the possibility of flotation is a real problem along the entire length, and (c) that once laid access to them for repair, maintenance and inspection is both difficult and very costly.

Another point is that the 'spread' is concentrated in a relatively short section of the route, with all operations required for the completion of the work and its acceptance being done in a set sequence and in the minimum of time consistent with the mandatory standards being achieved. These matters, as well as those related, must be catered for at the design stage of the pipeline. Such matters that require special attention are those of having to abandon and later recover the pipeline—during bad weather, for example—and of ease of access for divers or remote controlled vehicles (RCVs) where periodic visual inspection will be necessary.

Preliminaries

The route selection of a submarine pipeline is based on the result of sea-bed surveys carried out, generally, by equipment using sonic techniques. Video equipment may also be used in selected areas, if necessary in conjunction with the sonic equipment.

The object of the survey is to determine a route which:

(a) Will give a wide berth to any major sea-bed obstruction, a wreck for example;

(b) Avoid where possible large rock outcrops or where they are known to exist and cannot be avoided to determine a suitable route through or over the outcrop. Such a route through or over an outcrop may of course require some work to render it suitable;

(c) Will provide, if the pipeline is to be trenched, a route over material that will permit the effective use of the equipment that it is proposed to use for the trenching operation, or if the pipeline is not to be trenched, will result in an alignment that avoids as far as is practicable the incorporation of any spanning by the pipeline.

The initial route may be principally determined by basic parameters that are independent of any consideration of construction or hydraulics. These are:

(a) The views of fishermen who will wish to discuss with the pipeline operator the means by which the effect of the pipeline on any prime fishing grounds can be minimized or eliminated; this can result in a modification of a proposed route.
(b) The development plans of a third party to whom a licence to develop a 'block' to be crossed by the pipeline has been granted.
(c) Matters which are considered by the authorities to be of national importance.

Design

There is no basic difference in the method of designing a submarine pipeline and a land pipeline. The same considerations of pressure retention apply and Barlow's Formula is used in all normal cases. The standard design factor of 0.72 is applied, except to that part of the pipeline designated the riser. The riser is the vertical section which extends from the sea-bed to the deck of the installation and for which it is normal, in the UK, to use a factor of 0.60.

There are, however, a number of factors which require special consideration in the case of a submarine pipeline:

(a) Negative buoyancy. The effects of lift and drag must be considered and a weight per unit length calculated that will be sufficient to maintain the pipeline stable on the sea-bed. In large-diameter pipelines the weight is obtained by the application of concrete coating; in smaller diameters the weight is sometimes immediately available from the pipe weight, but occasionally it may be necessary to select a wall thickness slightly heavier than the pressure considerations require in order to obtain the weight economically. Factors in the determination of the negative buoyancy are the speed and direction of the currents that will act upon the pipeline, particularly during the construction period when it is empty. For a gas pipeline it is necessary to consider that the empty condition will apply throughout its operating life.
(b) Laying stresses. When laid by the conventional method from a lay barge a pipeline is subjected to very high stresses where it passes through the over bend, at the laying end of the barge, and at the sag bend where it reaches the bottom. The stresses can exceed the specified minimum yield stress of the steel and approximate to actual yield, even if not moving into the plastic zone. There are different views amongst designers and metallurgists about how far into the plastic zone the designer may go without producing lasting and injurious effects on the steel.

(c) Metallurgy. The chemical composition of the line pipe steel has to be compatible with the service of the pipeline. It has also to be so balanced as to ensure the production of satisfactory welds. Normalization of the heat-affected zone (HAZ) on each side of a weld may be necessary to avoid the steel of the area being left susceptible to cracking by any of a number of processes, principally hydrogen-induced.

Construction

Laying

There are now four generally accepted methods of laying submarine pipelines. Those prominent in the North Sea operations are:

(a) Conventional lay barge in which the pipeline is guided to the bottom over a ramp fixed amidships or over a 'stinger' which is attached, fixed or articulated, and made of steel tubulars and incorporating rollers. The stinger extends behind the barge and is adjusted to cater for the particular circumstances of the pipeline being laid (Fig. 13).

FIG. 13. Lay barge. *SEMAC I* is a third-generation lay barge, constructed in the fashion of a semi-submersible. The pipeline is welded, the weld radiographed and the field joint protection applied at individual stations on the barge, before being passed over a stinger, at the rear end of the barge and visible in the photograph, to the sea-bed. The line pipe is normally delivered to the barge having been 'double jointed'. In good conditions the barge moves forward every ten minutes or so when laying. It has a resident diving capability which operates under saturation conditions. (Photograph courtesy of Brown & Root.)

(b) Reel barge, which as the name implies has a length of pipeline coiled on a reel. The pipe is paid out as the barge moves forward. There is a limit on the diameter of pipe that can be handled in this way and of course on the length, but as an example a modern barge of this type can take more than five miles of 16-inch diameter pipe on a reel of 54 ft hub diameter and 82 ft flange diameter (Fig. 14).

(c) Bottom tow. In this method sections of pipeline are constructed onshore, buoyed in such a way that they will be just positively buoyant, and then pulled into position by surface craft. When in position the buoys are removed, allowing the pipeline to settle on the bottom. It has been shown in practice that alignment and the matching of ends for the purposes of connection present no undue difficulties, although the actual connection of one length to another requires some specialist equipment. It is also necessary that a detailed survey of the route is carried out prior to the tow in order to ensure that any serious obstructions are avoided.

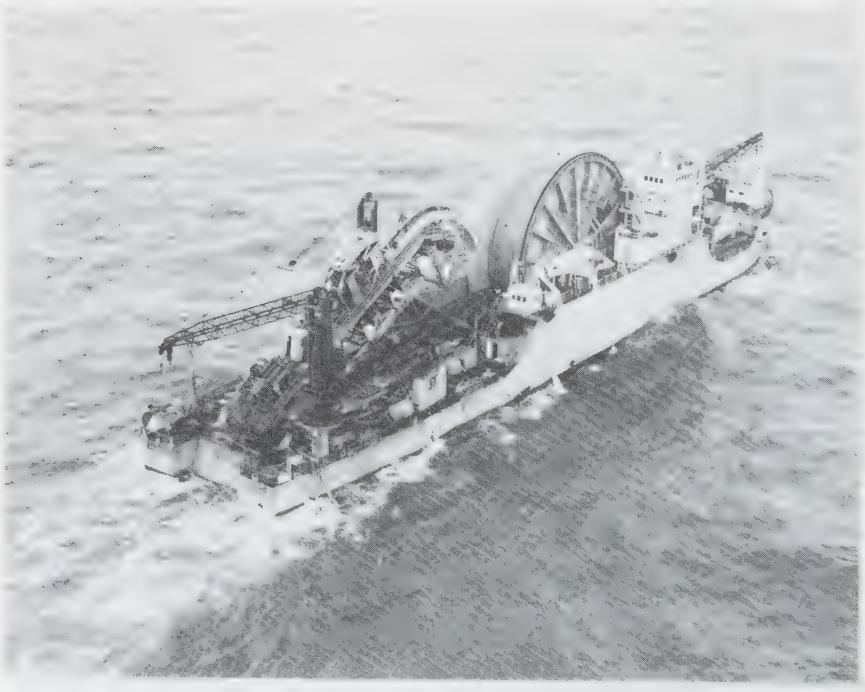

FIG. 14. Reel barge. *Apache* is a reel ship which has performed several tasks in the North Sea. The method of operation is described in the text. The laying mode is one of continuous operation interrupted, under normal circumstances, only when the installation of anodes is necessary.

The dimensions of the ship are 400 ft by 70 ft, and the unladen weight is 7040 tons. She is capable of operating in seas of up to 15 ft wave height. The abandonment and recovery system of the pipeline when Force 7 to Force 8 weather conditions interfere is by conventional means, using a constant tension winch capable of 300 000 lb tension. (Photograph courtesy of Santa Fe (UK) Ltd.)

(d) Surface tow, where the pipeline is constructed onshore, buoyed to float on the surface, manoeuvred by tugs into position and sunk on its required alignment. This system is used for the laying of pipeline 'bundles' in which a number of pielines are fastened together and then enclosed in an outer casing. The whole assembly is towed to position and sunk on the alignment.

Preparation

The preparation of the joints of pipe for incorporation in a submarine pipeline requires the application of an anti-corrosion coating, the attachment of sacrificial anodes and, unless the laying is to be done by the reel barge method or other considerations make it unnecessary, the application of a coating of concrete. In some cases it is necessary to attach buckle arresters. Buckle arresters, as the name implies, are to prevent a buckle propagating over a length of pipeline greater than the distance between the arresters. Buckles in submarine pipelines are initiated as a result of pressure or of bending, though generally by a combination of both. The anti-corrosion coating which may be one of a variety of materials is sometimes applied at the pipe mill. Some modern coatings, e.g. fusion-bonded epoxy, require special equipment for their application and so have to be applied at a pipe-coating yard equipped for the process. At the same yard it would be usual to attach or apply as appropriate, the remainder of the preparation.

Some of the conventional lay barges are capable of taking 'double joints' of pipe. For that operation joints are welded together in pairs at the coating yard prior to the application of the coating and by this method the amount of welding required offshore is reduced by approximately 50 per cent. This allows a higher laying rate to be achieved than would otherwise have been possible.

Inspection

Radiography is used for the inspection of welds, with the requirement that all welds are subject to this requirement. Ultrasonics are sometimes used as a supplement to the radiographic processes. A special requirement of this radiography offshore, and which is coupled with the need for speed, is the ability to 'bomb hot and read wet' obtaining sufficient definition to detect any defect.

Testing

The integrity of submarine pipelines is tested in the accepted manner by the application of a hydrostatic test. In a 24-hour test, which is the norm, it is necessary to demonstrate that any variation from laid down criteria is unconnected with a leak. The pressure requirements are always related to sea level.

Control

Control of a submarine pipeline system is effected with the use of microwave or for the 'over the horizon' type of operation, a tropo-scatter arrangement in

which radio waves are reflected from the atmosphere above the earth to the control centre receiving apparatus. Pipeline integrity monitoring is performed as a function of control with the object of detecting any leak that may occur. It is normal to monitor temperature, pressure, and throughput continuously at the main control centre, which may be situated offshore or on land, and to have the read-out duplicated at a second monitoring centre.

Specialist Equipment

The nature of a submarine pipeline system and the need to maintain, inspect, and possibly repair it dictate the need for certain sophisticated equipment. Amongst such items are:

(a) *Remote controlled vehicles* (*RCVs*) (Fig. 15)
In essence these are remotely controlled television sets used for inspection purposes. The depth of water in which it is necessary to operate and the need to orientate the camera involve the most complicated instrumentation.

FIG. 15. RCV. The RCV 225 is a remotely controlled underwater vehicle, 50 cm in diameter, and in operation deployed from an underwater cage suspended from the surface. This effectively de-couples ship motion from the vehicle. It is equipped with low-light television and a 35-mm still camera. Applications consist primarily of simple underwater viewing tasks such as those in pipeline laying and diving monitoring activities. (Photograph by Sub Sea Surveys Ltd.)

(b) *Mechanical connectors*

Underwater welding has been developed to a fine art, but occasionally if only for emergency or temporary repair purposes, mechanical connectors must be used. There are a number of types relying in some cases on metal to metal seals. Some of the types used in North Sea operations are illustrated below (Fig. 16(a), (b), (c)).

(c) *Welding*

There are a number of methods and a variety of associated equipment that have been developed for welding under water. In one system and up to certain depth limits special stick electrodes can be used. Another system, also with a depth limitation, utilizes a transparent box containing a gaseous atmosphere and the facility for a diver/welder to perform welding in the dry by putting his arms into gloves sealed to the side of the box whilst he remains outside in the wet.

Some of the most usual methods of deep water welding, however, are:

(i) Hyperbaric welding, where a habitat large enough to contain the diver/welders and with the facility of being able to be placed around the work, e.g. pipe ends, and maintained dry. The pressure within the habitat is maintained at or slightly above that of the surrounding environment, and so places those inside under that pressure.

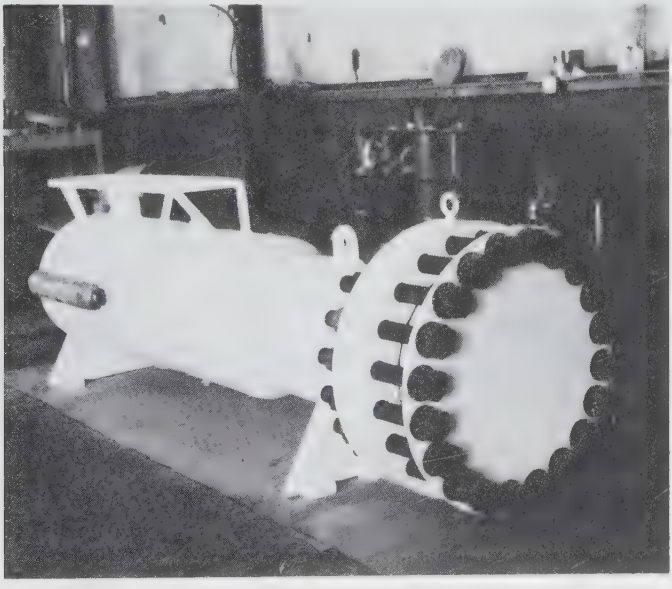

FIG. 16. Connectors. Connectors of the type illustrated are for the purpose of making mechanical, as opposed to welded, connections of two ends of pipe. Certain types of connectors incorporate a ball joint which allows misalignment of two ends to be catered for when the connection is being made.

(a) The Mk IV Hydrocouple/Misaligning Flange. (Photograph courtesy of Hughes Offshore, a Division of Hughes Tool Company Ltd.)

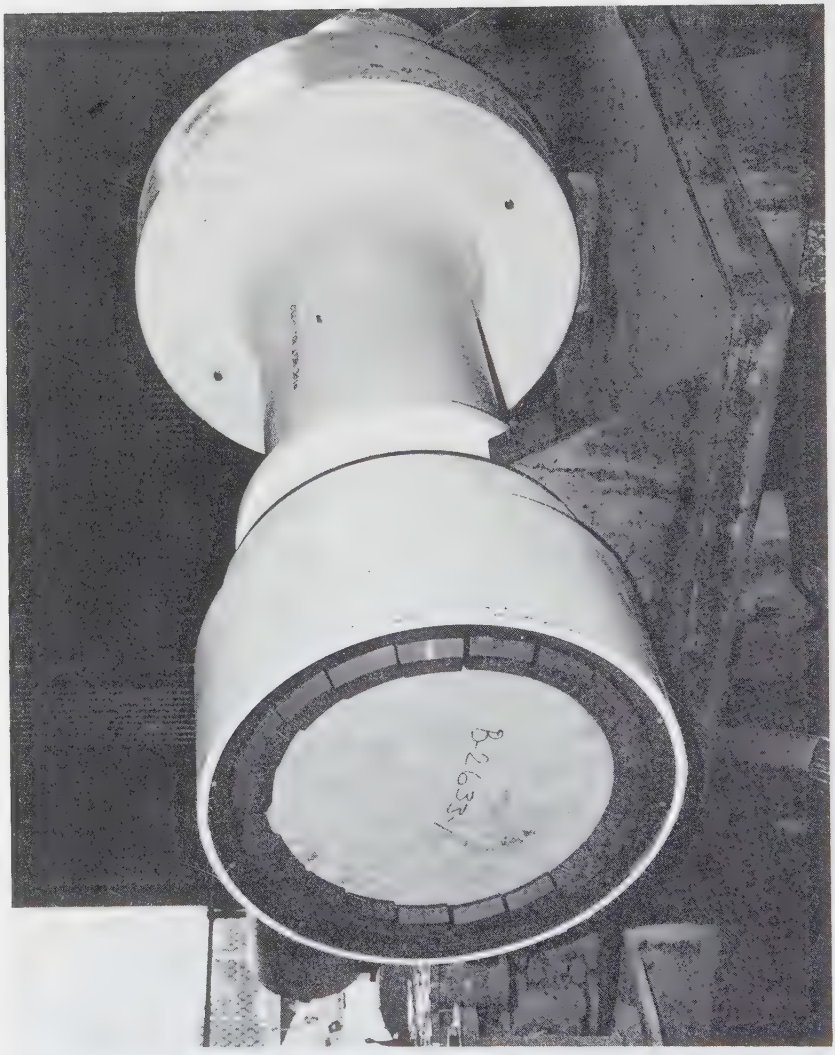

FIG. 16 (b) 24-inch Collet connector and swivel assembly. (Photograph courtesy of Cameron Iron Works, Ltd.)

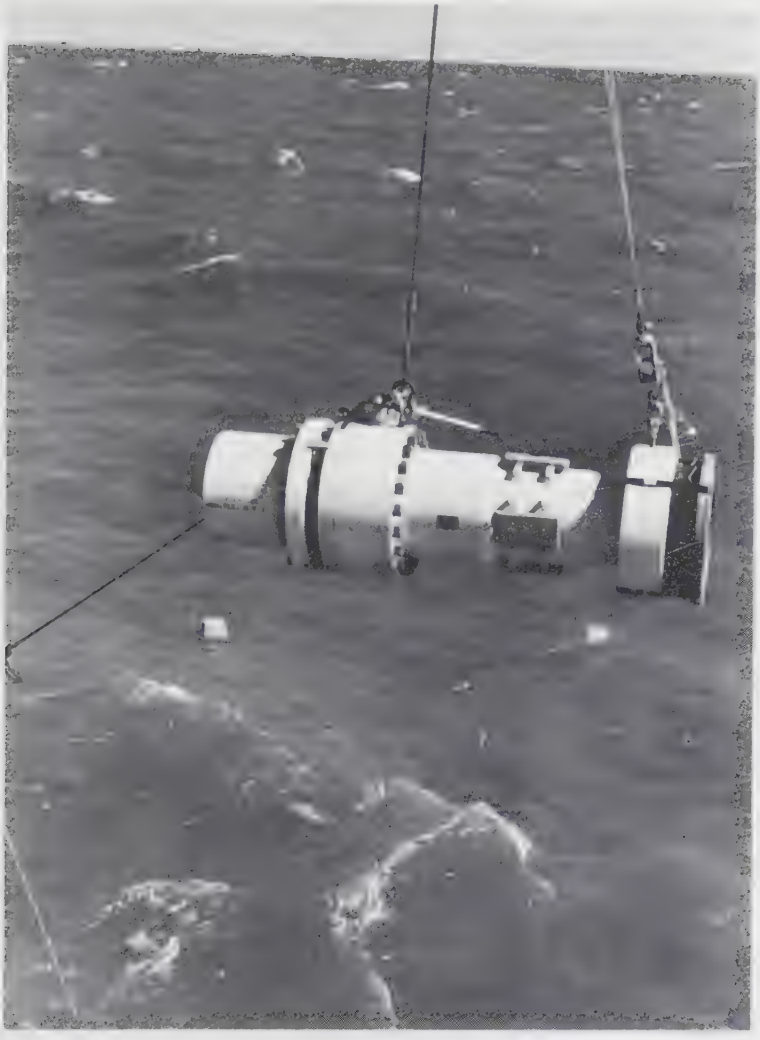

FIG. 16(c) 'Gripper' connector. (Photograph courtesy of Premaberg (Great Britain) Ltd.)

(ii) One-atmosphere welding; in this system the habitat has to be sufficiently robust to withstand the external pressure at the location and permit the diver/welder to work under similar atmospheric conditions to those which would be experienced if working at the surface. Obviously no decompression facilities are required for the diver/welders engaged in this type of operation.

Trends

The trend of offshore operations is towards deeper and deeper waters. Submarine pipeliners have to have this in mind and keep an eye on what waters

in excess of 1000 ft mean when the laying, inspection, and repair of pipelines have to be undertaken. Already pipelines have been laid in waters far in excess of 1000 ft and with surprising accuracy. External inspection of such lines has of necessity to be performed in the majority of cases by RCVs, though the present generation of manned submersibles -as used for inspection during the laying operation—are far from redundant as yet.

A pipeline in very deep waters is unlikely to be damaged in a way that one in relatively shallow water is likely to be, such as by anchors. Nevertheless, the possibility must exist of some form of a repair being required, and it is the availability of equipment that will be capable of carrying out such work that is a cause for concern to those who visualize having to operate in those extreme depths. That connectors, of a mechanical type, either have been or can be developed is accepted, as also that the capability exists of attaching them either by remotely controlled methods or with the minimum of diver intervention. It can be, however, that those operations will be easiest: the difficulty is going to be presented by the operations that will have to take place before such connectors are attached. Each pipeline will provide its own unique problem, but a case easy to imagine is one in which it is necessary before effecting a lasting or temporary repair, to evacuate the line, cut out the damaged portion, cut and prepare the pipe ends, determine the shape and size of the spool piece and when fabricated lower it and effect the connection. All this in very deep water requiring strong artificial light to allow surface monitoring by closed-circuit television, and possibly requiring the prior removal of some sea-bed material.

Another trend developing—also with deep water operation in mind—is a means of laying pipelines by the 'J' method (see M. R. Benefield). This requires the section of the pipeline to be held vertically on the purpose-designed barge, so reducing the number of sections at which a field joint may be made and prepared to, usually, one. This necessitates maximum speed in all operations, particularly welding, and for that reason a system of electron-beam welding in which a speed of some 3 5 cm/sec can be achieved on all thicknesses normally used in submarine pipeline application may be the answer.

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8

Transportation by Sea

By G. A. B. KING

HISTORY

The modern oil industry traces its beginnings to an accidental strike in Pennsylvania in 1848 and, more positively, to Drake's Titusville discovery 11 years later. In 1861, two years after Drake drilled his well, the first cargo of American oil to England was shipped in barrels on board the brig *Elizabeth Watts*. Twenty-four years later a ship called the *Glückauf* was built in the River Tyne, specifically for carrying oil, and for the first time the hull was used as a container for the free liquid instead of as a box to hold barrels. The *Glückauf* had her engines aft, leaving a clear, uncluttered tank space, and was in fact the prototype oil tanker. She could carry 2300 tons. Subsequently, other ships were built exclusively for carrying oil, many of which had the engine amidships in the manner of an ordinary cargo ship. In addition, conventional cargo ships were converted for the carrying of oil in bulk by fitting circular or rectangular tanks into the holds.

But the *Glückauf*, ahead of her time, had shown the way and by the First World War the oil tanker had become a recognizable type with engines and boilers aft, resulting in a short propeller shaft which did not have to pass through the cargo compartments. Ships were then quite small, perhaps up to about 8000 dwt, driven by simple reciprocating steam engines and coal-fired Scotch boilers. Between the wars tanker design was refined but did not alter fundamentally. For economic reasons the marine diesel engine came to be preferred by most owners, and the size of ships stabilized around 12 500 dwt, although there were a few larger than this. Until the Second World War the general pattern in the oil industry was to refine most crude oil at or near the production areas and to transport the refined products to overseas markets by tanker. The need for shipping flexibility and the wide variety of ports to which all ships had to trade under such circumstances limited the size of the ships to about 12 500 dwt and 27 ft draught. The typical general purpose oil tanker at the outbreak of the Second World War was powered by a heavy oil engine of 3500 hp and had a service speed loaded of 11 knots. During the Second World War the Americans designed a standard tanker of 16 000 dwt and 15 knots loaded speed, powered by a turbo-electric installation. This was the famous T.2 design, of which more than 500 were built, and which did so much to enable the international oil industry to deal with its immediate post-war ocean transportation problems.

After 1945 the shape of the world oil industry began to change and refineries tended to be built near markets rather than at production centres. This meant that crude oil formed a greater proportion of the cargoes to be transported, and tanker fleets began to split into two distinct categories. Some ships were designed specifically for crude haulage and some for products handling. Developments in engineering and naval architecture permitted bigger ships to

be built, and these had advantages in the crude oil trade. The products carrier still faced the same restrictions in the wide variety of ports to which she traded, but for crude carriers some of the restrictions could be overcome. Since the cost per ton-mile went down as the size of the ship went up, there was unquestionably an incentive to build bigger. In the early 1950s the first so-called 'supertankers' were commissioned. They were ships of between 25 000 and 32 000 dwt but they were quickly followed by others of 40 000, 50 000, 60 000, and then 80 000 dwt.

By the mid-1960s the 100 000 dwt ton barrier had been broken. The almost insatiable demand for oil-based energy in the late 1960s coupled with the closure of the Suez Canal led to a sweeping series of shipbuilding programmes, so that by the end of 1973 some 357 VLCCs of over 200 000 dwt were trading and another 470 were on order for delivery by 1977. The largest tanker was almost 500 000 dwt and there was talk of the 1 m dwt tanker.

Overall the world tanker fleet had grown from about 150 m dwt at the end of 1970 to 213 m dwt at the end of 1973 and the tankers on order were projected to increase it to over 400 m dwt by the end of 1977—an increase of 166 per cent in seven years!

In October 1973 the bubble burst. The OPEC countries asserted themselves and, almost overnight, quadrupled the price of crude oil. Inevitably oil demand was affected and in a brief time supply of tanker tonnage to carry oil on the long haul routes vastly exceeded demand for it. By late 1974 the surplus of supply over demand was about 100 m dwt and a surplus of varying size has remained ever since.

In the products trades the average new tanker size has increased from about 25 000 dwt in the late 1960s to around 32 000 dwt for 1982/3, although some considerably larger tankers are being built to handle product exports from the new OPEC refineries in the Middle East. All these modern products tankers are sophisticated and capable of handling a large number of grades without risk of contamination.

The current world tanker fleet includes some ships that are laid up and many that are slow steaming. The total world tanker fleet is set out in Table I below and shows that in terms of tonnage over half the fleet is in the VLCC category and that oil company owned tankers account for some 40 per cent of the total tonnage.

TABLE I

Size/Ownership Summary Existing Fleet

Size group Dwt	Oil company owned		Privately owned		Total	
	No.	Dwt	No.	Dwt	No.	Dwt
10–24 999	393	6 925 828	296	5 561 027	689	12 486 855
25 44 999	336	11 020 147	445	14 725 971	781	25 746 118
45–79 999	178	10 889 206	336	21 846 457	514	32 735 663
80 199 999	194	23 819 665	375	41 033 841	569	64 853 506
Over 200 000	242	66 917 177	347	92 631 806	589	159 548 983
Total	1 343	119 572 023	1 799	175 799 102	3 142	295 371 125

TABLE II
Size/Ownership Summary on Order

Size group Dwt	Oil company owned		Privately owned		Total	
	No.	Dwt	No.	Dwt	No.	Dwt
10–24 999	49	899 600	30	497 900	79	1 397 500
25–44 999	29	1 000 500	76	2 670 300	105	3 670 800
45–79 999	24	1 416 000	21	1 265 400	45	2 681 400
80 199 999	15	1 564 700	12	1 156 500	27	2 721 200
Over 2 000 000	3	853 000	1	313 000	4	1 166 000
Total	120	5 733 800	140	5 903 100	260	11 636 900

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Table II gives information on the sizes, numbers, and ownership of tankers on order.

DESIGN AND CONSTRUCTION

Hull Form

Whether of a quarter million tons deadweight designed to carry crude oil or one-tenth of that size and built for the more demanding products trade the ocean-going tanker is basically a strong metal box of subtle, but not usually fine lines, with a power unit and control system at the after end. In designing the ship the chief parameters to be defined are the service requirements, the limiting dimensions and the economic or acceptable speed. The service requirements will determine whether the ship is to be a large simple one to carry crude oil between a limited number of ports or a smaller unit for handling either clean or black refined products. The limiting dimensions are draught, beam, and length, and once settled these largely determine the deadweight which the hull can lift. The depth must be sufficient to provide in conjunction with the other dimensions the required volumes of cargo and segregated ballast. Depth must also be sufficient to allow the desired draught to be obtained without submerging the Plimsoll line. An economical power in relation to the required deadweight and speed is obtained by careful selection of the hull form. A form which is relatively short and full will be cheaper to build than a longer, finer ship, but could require excessive power to achieve the required speed. The naval architect's problem, given these parameters, is then to design a strong box girder which will withstand the stresses imposed upon it by the sea. A shallow ship of low draught for a given tonnage is operationally attractive but is more expensive to build than a deeper ship. The problem is to strike the correct compromise between these interacting factors. Table III shows typical dimensions of ocean-going oil tankers.

Layout

A typical layout for a ship of about 220 000 dwt is shown in Fig. 1. The hull must contain its liquid cargo intact from intrusion by the sea or from leakage

TABLE III

Size, dwt	Length Overall, M	Extreme Breadth, M	Draught, M
16 000 (T.2)	159	21	9
24 000	171	24	10
50 000	227	30	12
74 000	244	37	13
100 000	273	39	15
210 000	326	48	19
310 000	345	53	24
500 000	414	63	29

outwards, and the design of the inside of the container must be such that the liquid does not cause the whole to become unstable. The result is that the tanker hull is subdivided by longitudinal bulkheads, normally two in number, and transverse bulkheads which may number from five to 11 depending upon the ship's service requirements. The egg-box pattern is clear in the figure. This subdivision reduces the free surface effect of liquid moving about inside the tanks and provides segregation between different grades of cargo. The layout of tanks in new ships should also conform with IMO (International Maritime

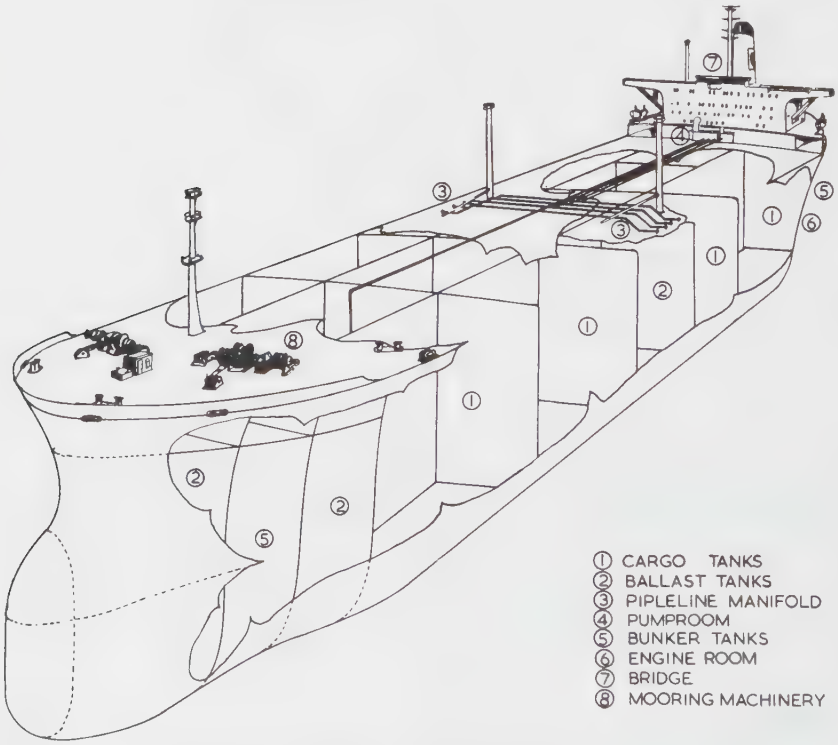

FIG. 1. Typical layout of a 220,000-dwt tanker.

Organization) requirements for minimizing pollution. These regulations limit the size and thus determine the minimum number of cargo tanks so that oil outflow in collision or grounding is within prescribed limits. IMO further requires that sufficient ballast space is provided in segregated tanks alone to achieve a suitable ballast draught. A minimum ballast draught of $0.02L + 2$ metres is given. These ballast tanks are required to be placed in protective locations, and minimum proportions of the areas of side shell and bottom are given. The intention of the segregated ballast requirement is to avoid as far as possible the cleaning and ballasting of oil tanks and thus prevent the pollution consequent on the discharge of ballast contained in oil tanks. These regulations are described in International Convention for the Prevention of Pollution from Ships and 1978 Protocol (MARPOL). They have had far-reaching effects on the design of tankers.

Liquid cargo can be moved from tank to tank or in and out of the ship through a system of pipelines passing along the tank bottoms and along the decks, and through a pump room normally located at the after end of the tank range. The cargo tanks are separated from the ends of the ship by cofferdams extending for the depth of the hull. The machinery space is placed aft for reasons of economy and safety, and it is now common practice, even in the largest ships, to place all the accommodation and the navigating bridge above the engine room. The space forward of the cargo tanks and cofferdam contains cable lockers, bunker storage space, and the fore peak tank. Some products carriers may have a dry cargo hold for the carriage of packed cargo.

The distribution of cargo, ballast, and bunker tanks is carefully arranged to give the required trim in loaded and ballast conditions without excessive stress.

Propulsion Machinery

The choice of the main propulsion machinery for oil tankers lies traditionally between boiler/steam turbine and slow or medium speed diesel engine installations. In selecting the main propulsion machinery the shipowner considers the power required, the capital cost, the installation size and weight, running costs, and the maintenance and repair requirements. The rising price of fuel oils from 1973, reaching fivefold by 1980, became an increasingly dominant factor in the machinery selection process.

The dramatic rise in fuel oil costs had three main effects. The first was to lower the optimum speed for new tanker designs, and therefore the power requirements. The second was to favour the more thermally efficient machinery systems. The third was to worsen the quality of residual fuel oils used by the marine industry as the refining processes were adjusted to give a higher proportion of the more profitable distillate products.

The diesel engine manufacturers, with the inherently more efficient engine, responded by increasing the engine power range to meet all tanker requirements, by increasing the diesel engine efficiency still further, and by improving the diesel engine's ability to use poorer quality fuels. As a result the diesel engine, mainly in its slow-speed form, has dominated the new building scene for tankers ordered after the mid-1970s. It is available with powers up to 35 000 kW for single units and with specific fuel consumption down to 180–185 grams per kW hour.

In addition, the higher fuel costs have justified more complex, higher first cost machinery systems aimed at maximizing the energy recovery from the fuel oil. For the diesel engine this includes the use of waste heat recovery boilers for electrical power generation and domestic services, shaft-driven generators for electrical power and gearing for optimizing propeller speeds.

Increasing costs of liquid hydrocarbon fuels have led to the consideration of other fuels. For a tanker coal and coke, or dispersions of these in oil are possibilities. These could be used for firing the boilers of boiler/steam turbine installations, and in the longer term, using fluidized bed combustion, for fuels for combinations of steam and gas turbines. While suitable 'all liquid' fuels are available at competitive prices the change to these types of installation will be slow, but coal and coke as alternative fuels do have a potential for the future.

Auxiliary Machinery

Whichever propulsion machinery is chosen for a tanker, supporting auxiliary plant will be required for cooling, lubricating, fuel preparation, and similar services. In addition there will be a need for equipment to support the hotel requirements of the ship's crew such as air-conditioning, galley, provision refrigeration, and laundry. All these services are generally electrically driven with power provided typically from diesel or steam alternators of about 1500 kW capacity in a typical VLCC. The diesel-engined vessel would traditionally have used diesel engines for electrical generation purposes also, but in recent years with the trend towards more fuel efficient ships increasing use has been made of steam alternators. Such machinery would be supplied with steam generated in a heat exchanger fitted in the exhaust of the main engine to recover the waste heat of its exhaust gases.

The electrical power demand of any tanker is always strongly influenced by the consumers not directly related to propulsion, and the tendency is for this demand to rise as new legislation, crew, or cargo requirements are catered for. It is important that such factors are fully investigated during design of a new ship's plant as they may outweigh some of the basic propulsion criteria. For example, the need to heat cargo may predict the boiler capacity rather than the main engine requirements, or the installation of an inert gas system may require that special attention is paid to electrical control systems.

Cargo Handling

Selection of auxiliary plant is partly conditioned by the main cargo pumping equipment in which the pumps themselves may be driven by diesel, steam, or electric power. Cargo is loaded into the tanker by being either pumped or gravitated from the shore through flexible rubber hoses or steel pipe gantries and along the ship's own pipeline system. When discharging, however, the shore can be of no assistance to the ship, which must pump her own cargo. The pumping system is important therefore, and in all crude carriers is located in a pump room at the after end of the cargo tanks. The modern products ship also has her pump room in this position, although in earlier classes a single pump room or two pump rooms were normally located within the tank range, providing a useful and positive segregation of dissimilar cargo grades. Because of the distance between boiler room and pump rooms these older ships could be equipped only with rather low output reciprocating pumps driven by low

pressure steam. In the more modern arrangement high capacity centrifugal pumps are located between the cargo spaces and the engine room bulkhead. In this position they can be driven easily by any suitable prime mover sited in the forward end of the engine room, and are connected by shafts passing through gas-tight seals in the dividing bulkhead.

For large crude carriers it is sometimes stipulated that the cargo pumping capacity should be 10 per cent of the vessel's deadweight, but in very big ships this results in a discharge rate much higher than most shore installations can receive. Another approach is to lay down the time in which a standard discharge should be completed, say 15 h. If the latter requirement is accepted the pumping capacity will be somewhat less than 10 per cent of deadweight, but in practice ship rates are usually somewhere between the two. A typical cargo pumping installation in a crude carrier of 200 000 dwt would consist of four single-stage centrifugal pumps driven by steam turbines. Each would be capable of 3000 tons of crude oil/h delivering at 100/125 psi at the ship's rail. For stripping (or draining) the last of the cargo the ship would have one or two steam-driven vertical duplex reciprocating pumps of about 350 tons/h capacity. In addition, two centrifugal pumps of about 3500 ton/h capacity of sea water would be used for handling segregated water ballast into or out of the ship, supplemented by at least one water-driven eductor for stripping ballast tanks. A modern products carrier might be equipped with four steam turbine driven single-stage centrifugal pumps with self-priming arrangements and an exhauster permitting them to be used for stripping. These could be expected to be of about 950 tons (water) capacity each, or 750 tons/h handling kerosine, and would deliver at about 125 psi at the ship's rail.

Flow of cargo into and out of the tanks is controlled by valves either in the bulkheads in the case of crude ships fitted with a free-flow system, or in the pipelines in other ships. These valves in smaller older ships are hand-operated, but in modern ships may be mechanized and controlled at site or remotely (and usually hydraulically) from a cargo control room normally located above the main pump room. The level of oil in each compartment, formerly gauged through an open pipe at the crown of each tank, is indicated in modern ships by mechanical gauging devices reading out at the top of the tank or remotely in the cargo control room. The modern cargo handling system is designed to load and discharge cargo as economically and safely as possible, using the minimum number of men, and maintaining full control over every stage of the operation by providing essential data when and where it is most required. In the most sophisticated installations with centralized control over the entire valve, gauging, and pumping systems, it is possible for one man to carry out the entire operation on board ship, although for safety and security reasons this is seldom, if ever done. The senior officer in charge is normally backed up by one other officer and at least one rating.

Safety Arrangements

The International Maritime Organization (IMO), the maritime arm of the United Nations Organization, has over many years developed a comprehensive set of conventions which define safety, construction, and operating standards. For British flag ships the responsibility for applying the appropriate regulations rests with the Department of Trade. There are in addition safety

precautions specified in the International Safety Guide for Oil Tankers and Terminals, which are required because of the nature of the cargo. Crude petroleum and many of its products, for example, are volatile and readily give off vapour which may, in certain concentrations with air, be explosive. A ship which carries oil must therefore have adequate venting arrangements to clear away any vapour that may be evolved whilst the ship is loading or carrying cargo. Ventilation is usually through pipes leading from the crown of each compartment to a common header and thence vertically up the masts or samson-posts.

Alternatively, each compartment may have its own individual short stack vent rising two or three metres above the deck. This arrangement is thought by some to be more suited to product carriers where it is important to avoid cross-contamination of different grades of cargo by vapour leakage along a common venting system.

In order that a change of grade can be made or entry into a tank for repair work be carried out it is necessary for the tanks to be rendered gas-free after the discharge of cargo. This means that it will usually be necessary to wash out the cargo residues with either hot or cold sea water. This is done by means of portable rotating machines suspended in the tanks on the ends of rubber hoses through which water is delivered to the machines. Due to the increase in the size of cargo tanks in the bigger ships built in the last decade it became customary to fit fixed tank-washing machines in the tanks, since it was not possible to wash the tanks effectively with the smaller portable machines. The fitting of these fixed machines is now becoming more common on the smaller ships as well since this reduces the manpower required for handling the heavy hoses and machines, and is therefore more cost effective. The cargo pumps are used for the stripping of the wash water, and on completion of the washing cycle each compartment is ventilated mechanically by means of either portable air- or water-driven fans or a central fan blowing air through the cargo pipeline system. After the appropriate tests have been made the tanks can then be declared fit for a change of cargo grade or for entry for repair work to be carried out.

The ever present risk of fire or explosion can be reduced by the fitting of an inert gas system and at the present time such systems are mandatory for all new tankers of greater than 20 000 tons deadweight and for existing ships of greater than 70 000 tons deadweight. The inert gas is provided either from the exhaust gases from the main boilers or from a dedicated inert gas generator. In the case of the boiler flue gas system the gas is drawn from the boiler uptakes, washed, and cooled in a scrubbing tank and then passed to the cargo tank ullage space. The inert gas drives out the oxygen in this space and by reducing the oxygen content to below 8 per cent inhibits any fire or explosion from occurring.

New regulations imposed in 1980 require all new tankers over 1500 gross tons to be provided with fixed foam fire-fighting monitors spaced at intervals along the deck so as to enable them to deal with any spill fires that may occur.

Specialized Tankers

Some products of the petroleum industry are of such a nature that they require special handling, and when carried by sea call for custom-built and equipped

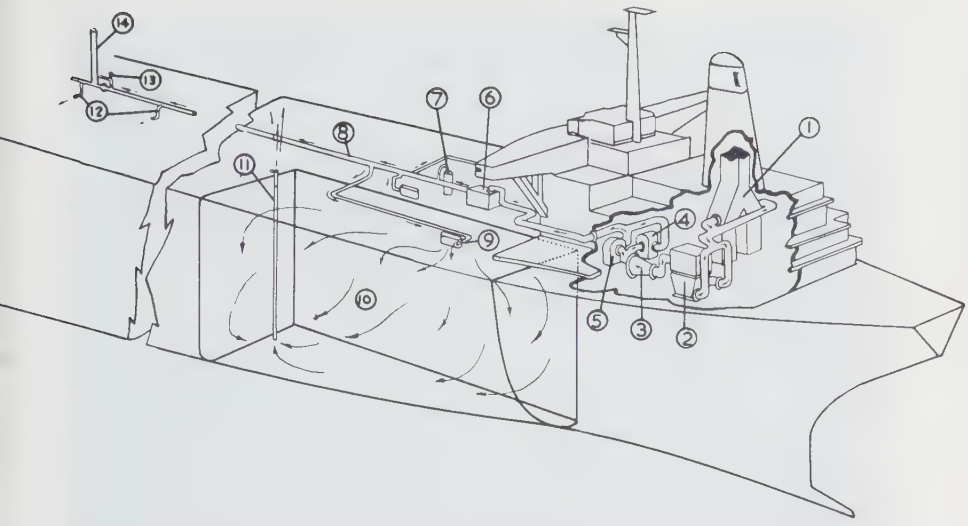

FIG. 2. Inert gas systems (drawing by Capt. Bruce Keer).

1. Boiler uptakes
2. Scrubber
3. Separator
4. Auxiliary fan
5. Main fan
6. Water seal
7. Oil seal pressure release
8. Main gas pipeline
9. Cargo tank branch pipe
10. Cargo tank
11. Purge pipe
12. Cargo tank branch pipes
13. Pressure vacuum valve
14. Mast riser

FIG. 3. BP's 25 000-ton tanker, *British Tay*, during her trials off the Swedish coast.

FIG. 4. BP's 270 000-ton tanker, *British Respect*.

FIG. 5. A 312 000-dwt tanker, *Universe Kuwait*, loading at an offshore terminal.

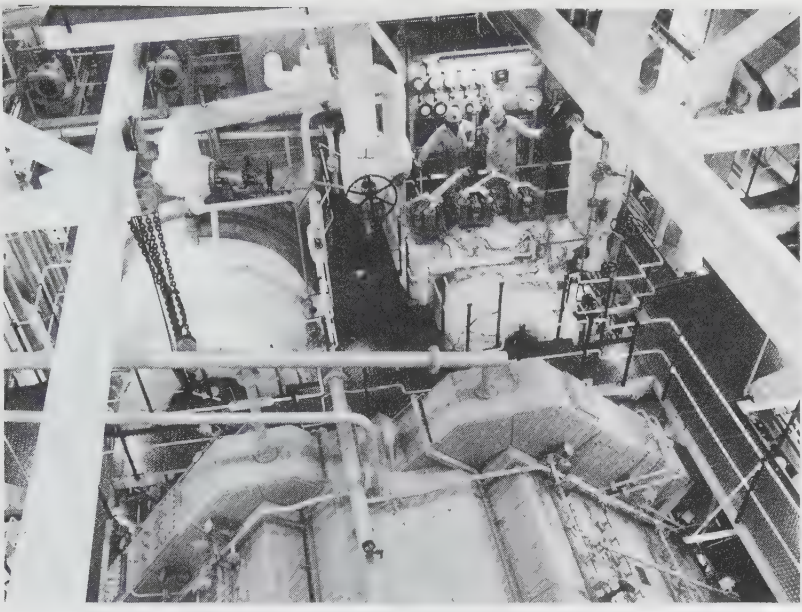

FIG. 6. General view of main engine room on board BP's 250 000-ton tanker, *British Promise*.

FIG. 7. Main engine room control console on board BP's 270 000-ton tanker, *British Respect*.

FIG. 8. Pump control room on board BP's 270 000-ton tanker, *British Respect*.

ships. Bitumen was perhaps the first of these cargoes for which tankers were specially designed. The bitumen carrier usually has smaller wing tanks than a conventional tanker and the high gravity cargo can be wholly contained in the centre tanks where it is partially insulated from the cooling effect of the sea by the wing tank cushion between. In addition the cargo tanks are fitted with an extensive heating coil system so that low pour point bitumen can be maintained at a temperature at which it is liquid. The ship's pumping system is also specially suited to handling hot, viscous liquid and the deck pipelines, along which cargo flows to or from the shore, are lagged and steam-traced.

Of greater potential economic importance are those ships designed to carry LPG (butane and propane), anhydrous ammonia, butylene or butadiene, or LNG (methane) and ethylene. LPG carriers are sometimes termed low temperature ships and those built for LNG as very low temperatures ships. Typically LPG cargoes are carried at around $-40\,^{\circ}C$. LNG, on the other hand, if carried at atmospheric pressure, must be cooled to below $-160\,^{\circ}C$. Some ships have been built to carry liquefied gases in semi-refrigerated condition under pressure. These have usually been substantially smaller than ships now in service capable of lifting more than 125 000 cubic metres.

Because of the low temperatures at which liquefied gases and some chemicals are carried the ship's hull can no longer serve as the direct container for the cargo, as in the conventional oil tanker. Instead the cargo is contained in large separate tanks built into the ship's hull. There are two main types of tank design, self-supporting and membrane. Self-supporting tanks are strong, rigid either prismatic or spherical containers of nickel steel or aluminium, secured within the ship's structure and surrounded by insulation such as polyurethane

foam or slabs. With membrane tanks the ship's hold is lined with several layers of insulation such as cross-laminated balsa wood with plywood facings. In addition to its insulating properties this performs the duty of bearing the full weight of the cargo which is contained inside a membrane tank of stainless steel, Invar or other suitable material fixed to the inside face of the insulation. It is imperative when carrying low temperature liquefied gases that any leakage of cargo is contained before it can reach the steel of the ship's outer hull.

Handling cargo of this type is a more sophisticated operation than with ordinary liquid cargo. Before loading, tanks must be purged of oxygen using an inert gas produced by the ship's own gas generator. They are then cooled down to receive the cargo. Refrigerating and re-liquefaction plant maintains the cargo at the required temperature on passage, and the boil-off is either re-condensed and returned to the tanks or, in the case of some methane tankers, used economically as fuel in ship's boilers. Discharge of cargo is carried out by means of deep-well pumps, two of which are located in each tank. Control of all cargo handling and tank preparation systems is normally centralized in a fully instrumented control centre amidships.

Chemicals, feedstocks, and liquid sulphur are also carried in specially constructed ships. Each commodity brings its own plant and procedural requirements, but in them all, as with liquefied gases, the primary essential is a high degree of control to ensure that handling and carriage of the commodity can be achieved efficiently, economically and, above all, safely.

ECONOMICS OF SIZE

Technical Ability to Build

It may be claimed that the most significant development in oil transportation since the *Glückauf* has been the growth in individual ship size during the past three decades. Until the immediate post-war years tankers were built as multi-purpose ships carrying mainly products from refineries in the production areas to markets. When required they also carried crude oil to those other refineries which existed near industrial markets. In either trade their dimensions were restricted, but even had the use of bigger ships been feasible, the knowledge and experience to design and build them did not then exist, and had to await the development of new techniques during the Second World War. Furthermore, it was not until after the war that engines of the higher power necessary were being built. The conjunction of a need and the ability to satisfy it occurred in the late 1940s and early 1950s, at a time when the oil industry's operating pattern was changing and much greater quantities of crude had to be moved over long distances.

Natural Limitations

As ships become larger they require deeper water in the ports to which they trade. Flexibility of choice is inevitably curtailed with increase in size, and the largest ships are severely restricted to a small number of deep-water terminals for both loading and discharging.

The Suez Canal imposed another restriction. At the time of its closure in 1967 ships could transit on 38 feet draught, but since it reopened in 1975 it has been widened and deepened to allow tankers of up to 320 000 dwt to transit in ballast and up to approximately 150 000 dwt laden. Even in the open sea there are restrictions upon the draught at which it is safe to operate ships in certain areas. Nevertheless, where all these restrictions can be accepted the advantages of larger ships can be considerable in lower freight costs.

Capital Costs

The capital cost of building tankers does not increase directly with size, and a large hull costs appreciably less per deadweight ton than a smaller one. In addition, the costs of machinery, accommodation, and cargo handling equipment do not greatly increase with size. As an example, whilst the price of a newly built 250 000 dwt tanker might be $75 m compared with $32.5 m for 80 000 dwt (say +130%), it would carry nearly three times the amount of cargo over the same route (1982 prices).

Operating Costs

Operating costs consist of insurance premiums, stores, repair and maintenance, manning costs, and administration. Insurance is related principally to deadweight tonnage and, to a lesser degree capital cost, and tends to reduce over size. Maintenance and survey costs vary.

To the operating costs must be added the voyage costs of bunkers, and port and canal charges. Bunker consumption does not rise proportionately with ship size. For example, a new 50 000 dwt motor vessel would consume 35 tons/day whereas a new 110 000 dwt motor ship consumes 54 tons/day; thus bunker costs reduce as size increases.

This of course relates to newly built motorships, whereas many of the existing VLCCs have much higher consuming steam turbine engines and can only become economical in today's market by slow steaming.

Port and canal charges are generally levied so that the unit cost is more advantageous to bigger ships and therefore the overall pattern is for unit costs to reduce per deadweight ton as size increases.

Freighting Comparisons

Freighting costs grow substantially as the length of the voyage increases. The comparisons assume single-port loading and discharge (Table IV). If the larger tankers make multi-port loadings then some of the advantage is lost.

Flexibility

There are now some 377 tankers in existence of over 250 000 dwt, including 28 of over 400 000 dwt. Although these ships have the benefit of reduced unit costs the rate of improvement begins to level off over 300 000 dwt. Against these improved unit costs must be set some disadvantages of operating very large ships. The capital investment in each tanker is high and the amount of shore

TABLE IV
Comparative Freighting Costs (1982)

Dwt	Freight cost/ton ($)		
	Mina-Rotterdam Suez/Suez	Mina-Rotterdam Cape/Seuz	Mina Rotterdam Cape/Cape
25 000	20.41	26.90	32.97
70 000	10.28	13.43	16.45
110 000	6.91	9.03	11.03
215 000*	—	7.29	8.89
270 000*	—	6.29	7.67
400 000*	—	5.47	6.57

Assumes full cargo with single-port loading and discharge.
Bunkers $165/ton.
Suez routes include Suez differentials.
* 10 k laden and ballast.

tankage involved in storing vast quantities of oil calls for further heavy capital investment. In addition the development and maintenance of ports capable of accommodating these ships is expensive and difficult.

To exacerbate these problems the overall control of the oil distribution network in recent years has become more fragmented. Major oil companies once controlled much of the crude oil supply system from the oilfield through to the refinery. Tankers were programmed as part of an integrated fleet to minimize transportation costs. This system has largely broken down with the majors lifting a smaller proportion of oil produced by OPEC countries, and increasingly large tankers are having to make two- or three-port loadings and discharges to avoid sailing with only a part cargo.

This has eroded some of the advantages of the VLCC and led to the development of a smaller type of crude oil carrier in the 75–100 000 dwt size range which can reap most of the benefits of size, and fits more closely the average parcel size now available in the Middle East. In addition tankers of this size can trade to the US East Coast, Australia, and other draught-restricted areas, and transit the Suez Canal fully laden. Tankers of this size range give the operators a much more flexible opportunity for taking most advantage of whatever conditions may prevail over the tanker's potential life span of 20 years.

OPERATIONS

Loading

Loading instructions for the forthcoming voyage are normally sent to a ship by radio prior to her arrival at the loading port. The quantity of cargo that can be loaded may then be calculated making due allowance for the weight of bunkers, stores, and fresh water that will be on board and for the loading regulations which govern how deeply the ship may be laden at all stages during the loaded voyage. Normally, the ship will have on board clean ballast water and much of this will be discharged to sea before arrival at the loading port, leaving on

board only the minimum weight required to keep the ship manageable during berthing operations. Once on the berth the remainder of the ballast water is discharged either into the sea or, if local regulations so stipulate, ashore. In the event that there has been insufficient time during the ballast voyage to clean sufficient tanks to provide clean ballast then it will be necessary to discharge all of the ballast ashore as it will be dirty (i.e. oil-contaminated). When the ship is alongside the berth the shore hoses are connected to the ship's manifold amidships and the cargo tanks are inspected and passed empty and fit to contain oil. The cargo lines on board are set, and when preparations have been completed the shore valves are opened and oil allowed to flow into the ship. In modern crude oil ships, the initial loading is very often concurrent with the discharge of the final quantity of ballast.

The cargo may be either pumped or gravitated from the shore and high loading rates are often achieved. For example, at the offshore terminal off Kuwait, a loading rate in excess of 15 000 tons per hour is possible with a gas turbine driven pump delivering crude oil 10 miles along a 48-inch sea-bed line. The loading rate is set by the ship, and it depends largely upon the capacity of the ship's venting system to deal with the displaced vapour (as cargo is loaded) and on the rate of liquid rise in the cargo tanks acceptable to those controlling the operation on board. It is common practice on large crude carriers to begin operations by opening all the wing cargo tanks to receive the incoming oil during the simultaneous deballasting of centre cargo tanks. When the wing tanks have been filled the operation is completed by loading the centre cargo tanks. Alternatively, centre tanks may be loaded first followed by wing tanks. The entire operation must be closely supervised so that overflow of oil is prevented, and this is especially so when topping off each cargo tank. Oil flow is controlled by manipulating the ships's valves either from the cargo deck or from the cargo control room. Gas from the incoming cargo is vented through the gas system clear of the ship. As compartments are filled the ullage, or space above the liquid in the tank, is measured by means of automatic ullage gauges that register the ullage either at the top of the tank or remotely in the cargo control room. By reference to the tank capacity tables (supplied by the shipbuilder) the volume of oil in each compartment is established. The temperature and the density being known, it is a simple calculation to estimate the tonnage or number of barrels loaded. When filling the last tank(s) constant reference is made to the loadline marks cut into the ship's hull on each side amidships. The ship must not be loaded deeper than a certain point on or near the loadline depending on the geographical location, the projected voyage, and the season of the year. The original estimate of the weight of cargo to be loaded and the total tonnage in the other compartments can indicate how much may be placed in the last tank(s), but the operation is completed to the appropriate marks so that the ship is not overloaded. When loading is finished all valves on board are checked shut, documents are prepared ashore after agreement between the ship and shore, and shore hoses are uncoupled and removed. The whole operation may take only twelve hours in a ship loading crude oil, and certainly would be considered slow if it took as much as twenty-four hours.

Handling products is naturally more complicated since the ship may be required to carry seven or eight different grades of oil. These may not all be loaded in the same port and frequently they will have to be discharged at

several ports. The stowage of each separate parcel must be carefully calculated bearing in mind the trim of the ship and stress on her hull when weights are placed on board or removed from it. It is quite normal to load two grades of oil simultaneously, but their lines and valves must be isolated from each other so as to avoid risk of contamination between the grades. Discharging plans must also be kept in mind at the time of loading to ensure that there will always be a sufficiently clean line and pump to handle the more vulnerable grades of oil being carried. Loading rates are substantially slower in the products trade, particularly with clean oils where rates are almost always under 1000 tons per hour. Equal care to avoid overflows is necessary, and this is especially the case when loading low-gravity products which require greater space for a given quantity and are consequently loaded higher in the tank. On completion of loading cargo samples are tested for quality before the ship sails.

Once a tanker has sailed from the loading port it is normal practice, after twenty-four to forty-eight hours, to retake the ullages of the cargo and recalculate the cargo quantity. At the same time water dips are taken in each tank so that any water that may have settled out of the cargo can be measured.

Discharging

Prior to arrival at the discharging port the ullages and water dips are again taken and the cargo quantity recalculated. There will have been during the loaded voyage, a certain loss of cargo due to vaporization. On arrival at the discharging port the ship's manifold is again coupled to the shore by means of hoses. As this is being done any cargo measurements required by the shore representatives are taken. When the preliminaries have been completed and the shore is ready to receive cargo, discharge is started using the main cargo pumps in the ship.

On crude oil ships it is normal to discharge several compartments at once, and the bulk discharge is continued until only a small quantity of cargo is left at the bottom of each tank. The main cargo pumps are then transferred to other full compartments without speed being reduced so that the bulk discharge rate is maintained. The small quantities of oil left in those tanks discharged earlier are then drained by using either the stripping pump or using cargo eductors. These may be discharged to another empty compartment from which they can eventually be discharged as bulk or directly to shore. During the bulk discharge it is common practice to crude oil wash tanks that are going to carry either departure or arrival ballast, plus one quarter of the remainder of the cargo tanks.

About halfway through the discharge operation water ballast is run into the ballast tanks or into cargo tanks designated to carry the departure ballast required before the ship sails. Regulations require that when the ship loads ballast in the cargo tanks it is to be loaded concurrent with the discharge of cargo from other compartments so that the gas atmosphere displaced in the tank(s) being ballasted can be compensated for by the vacant space being created in the tanks being discharged. In this way, the emission of hydrocarbon gases to the atmosphere is prevented, thereby avoiding atmospheric pollution.

Discharging of a product carrier is a more complex operation and it is restricted by the disposition of the cargo within the ship. It is clearly necessary

to take separate groups of tanks individually and discharge them through a clean line and a clean pump. At all times the trim of the ship must be reasonably maintained and it is not possible to achieve the same rates of discharge with refined products as with homogeneous bulk cargoes. In product ships, no provisions are made for separate ballast tanks and cargo tanks are used. This means that the ship is not normally ballasted until the discharge of cargo has been completed.

International legislation now requires that the majority of tankers be fitted with inert gas systems. That is, gases from the boiler uptakes are drawn off by powerful fans which transfer them to the cargo spaces via a scrubbing unit which washes and cools the gases. In this way the boiler exhausts can be used to fill the space in the cargo tanks that is vacated as the cargo is discharged. This will ensure that the atmosphere within the tank will always be oxygen-deficient so that combustion cannot be supported.

Tank Cleaning

On the ballast passage from the discharging port to the loading port some, or all, of the ship's cargo tanks are washed out with sea water. In the products trade this has to be done so that the ship may be presented at her next loading berth completely clean and fit to carry any cargo. In a crude oil ship it is only necessary to water-wash a proportion of the cargo tanks. That is, it is prudent to wash only those tanks into which it is intended to load the ballast that will be on board the ship when she arrives at the loading port. This is so that the water ballast, which will have to be discharged into the sea, will be clean and uncontaminated with oil. Other than these tanks it will only be necessary to wash tanks that have to be entered for an inspection or for maintenance.

In product ships the normal practice is to suspend portable machines inside the cargo compartments on the end of rubber hoses through which sea water is pumped at about 100–150 psi. The heads of the machines revolve much as a lawn sprinkler does, throwing high-velocity jets about the inside of the compartments and thoroughly washing them. Liquid collecting in the bottom of the tank is cleared away by the stripping pump or eductor. The whole operation, although mechanized, is fairly labour intensive, especially when a large number of compartments have to be washed on a very short sea passage.

On crude carriers the water washing of tanks is accomplished by using fixed tank washing machines that are permanently fitted in each of the cargo tanks. These operate more like a fireman's hose, and their nozzles rotate through 360 in the horizontal plane and through approximately 120 in the vertical plane. When the washing water is supplied to the machine the nozzle rotates through the horizontal plane and to each 360° rotation it will also move through approximately 2½ in the vertical plane. In this way all surfaces within the tank will be washed by the water jet from the machine at some stage during the washing cycle. The use of fixed tank washing machines reduces the amount of labour required for tank washing. The same fixed tank washing machines are used for crude oil washing of tanks concurrently with the discharge of oil.

Before a compartment is washed on a products or crude oil ship, it is normal practice to purge the tanks of hydrocarbon gases using the inert gas system.

This will ensure that any hydrocarbons in the tank are discharged to atmosphere and enables the tank to be washed in a safer atmosphere.

Oil Pollution Control

Tanker operations are very much dictated by the regulations contained in the International Maritime Organization (IMO) Convention for the Prevention of Pollution from Ships, 1973 and its Protocol of 1978 (MARPOL 73/78). This convention covers all aspects of marine pollution and pollution prevention comprehensively. For convenience, the regulations are contained in five annexes, which cover:

Annex I: Regulations for the Prevention of Pollution by Oil.
Annex II: Regulations for the Control of Pollution by Noxious Liquid Substances in Bulk.
Annex III: Regulations for the Prevention of Pollution by Harmful Substances carried by Sea in Packaged Forms, or in Freight Containers, Portable Tanks or Road and Rail Tank Wagons.
Annex IV: Regulations for the Prevention of Pollution by Sewage from Ships.
Annex V: Regulations for the Prevention of Pollution by Garbage from Ships.

Of these, Annexes I, IV, and V have the most direct effect on tanker operations.

Annex I

(a) Prohibits the uncontrolled discharge of *all* oils (persistent and non-persistent) anywhere in the world. It allows the controlled discharge of oil subject to certain parameters which are:

From cargo spaces
(i) the ship is not in a special area;
(ii) the ship must be proceeding on voyage;
(iii) the instantaneous rate of discharge must be <60 litres/mile;
(iv) the total quantity of oil discharge must be $<1/15\,000$ of the total quantity of the previous cargo for existing ships and $<1/30\,000$ for new ships;
(v) the ship has in operation an oil discharge monitoring and control system (where fitted) and a slop tank arrangement; and
(vi) the discharge must be >50 miles from land.

From machinery spaces
(i) as per (i) and (iii) above;
(ii) the ship is >12 miles from the nearest land;
(iii) the oil content of the effluent is <100 ppm; and
(iv) the ship has in operation an oil discharge monitoring and control system, oily-water separating equipment, and oil-filtering equipment.

(b) Defines the Mediterranean Sea, the Baltic Sea, the Black Sea, the Red Sea, and the Persian/Arabian Gulf as declared special areas. Both controlled and uncontrolled discharges of oil are prohibited in these areas (except in dire emergency) and the authorities of the countries bordering these areas are obliged to provide reception facilities for oil-contaminated effluents.

(c) Requires that from the entry-into-force date all tankers must operate under one of three categories, depending on the facilities they are provided with. That is:

New ships	Ship category	Existing ship
< 20 000 dwt	*Crude oil and product carrier*	*< 40 000 dwt*
> 20 000 dwt with [1] SBT/PL + COW	(allowed to carry either crude oil or product, or both simultaneously)	*> 40 000 dwt* with SBT
		> 40 000 dwt with [2] CBT + COW
* *> 70 000 dwt* with SBT		*> 70 000 dwt* with CBT for 2 years†
		40/70 000 dwt with CBT for 4 years†
20/30 000 dwt	*Product carrier*	*> 70 000 dwt* with CBT after 2 years†
> 20 000 dwt with SBT/PL	(allowed to carry product oil but prohibited from carrying crude oil)	*> 40 000 dwt* with CBT after 4 years†
	Crude oil carrier (allowed to carry crude oil but prohibited from carrying product oil)	*> 40 000 dwt* with COW

[1] SBT—segregated ballast tanks.

[1] PL—protective location (refers to SBT positioned at side where a collision might occur).

[1] COW—crude oil washing.

[2] CBT—clean ballast tanks.

* This category refers to ships that were ordered as 'new ships' under the original MARPOL. The 1978 Protocol amended the 'new ship' start date and the requirement from SBT to SBT/PL.

† That is, after the date that MARPOL 73/78 entered into force.

(d) Defined the requirements for ships operating SBT/PL, COW, or CBT systems and makes allowances for ships operating in specific trades or with permanent ballast tanks (i.e. sufficient ballast is *always* on board whether the ship is loaded or not).

(e) Requires tankers to operate LOT‡ and also to use the Oil Discharge

‡ LOT—load on top.

Monitoring and Control system when discharging effluents overboard. New ships must be built with the monitor installed. They are to be back-fitted on existing ships within three years of MARPOL 73/78 entering into force. In addition to monitors, machinery spaces effluents must pass through oily-water separating and filtering systems.

(f) Lays down requirements for the arrangements for piping used in the discharge of effluents overboard, and contains regulations covering the construction of tankers for the minimizing of oil pollution by laying down assumptions to be used when assessing damage conditions, hypothetical outflows of oil from damaged compartments, and the limitations of tank sizes. This includes sub-division and stability information.

(g) Lists oils that are covered by Annex I.

(h) Gives examples of the IOPP* Certificate and the Oil Record Book to be used.

Annex IV

Requires ships to be fitted with sewage plants so that only comminuted and disinfected sewage is discharged.

Annex V

(a) Prohibits the disposal to sea of all plastics (including synthetic ropes and plastic bags).

(b) Requires garbage disposals to be 25 miles from the nearest land (for materials that float) or 12 miles (for food wastes and 'sinkable' garbage), but these distances may be reduced to 3 miles if the garbage is first processed through a grinder.

(c) Stipulates that in Special Areas only food wastes can be disposed of and these must be 12 miles from land.

(d) Requires ports to provide garbage reception facilities.

Crews

In most countries oil tanker officers do not receive any specialized training early in their careers but, by lengthy experience, develop considerable expertise.

In the UK it is the usual practice for a tanker officer, regardless of seniority, to attend specialized courses covering all aspects of tanker operations. Internationally recognized regulations have recently come into force which require a certain level of formal training in the safety aspects of tanker operations, together with statutory minimum periods of tanker experience, before officers can occupy senior positions in either the Deck or Engineering departments on board tankers.

Ratings may not remain long in the oil trade but are encouraged to develop the expertise which in modern ships is more and more required of them. Because of the nature of her trade and the many possibilities for mechanization and automatic control even the largest oil tanker requires a small crew compared with other ships. Manning scales vary from country to country, but a

* IOPP—International Oil Pollution Prevention.

ship of 100 000 dwt nowadays probably goes to sea with about 12 officers and 20–25 petty officers and ratings.

In the UK a development known as General Purpose Manning means that all petty officers and ratings are trained to work anywhere in the ship, and former departmental barriers are dispensed with. This results in a smaller, better trained and more efficient crew.

Navigation

The navigation of oil tankers is no different from that of other ships, although in general terms they are amongst the best equipped navigationally. In very large ships, of course, there is constant concern for finding deep enough water to accommodate their very deep draught. Very large ships are less manoeuvrable than small high-powered vessels (such as cross-Channel ferries or warships for example), but are nevertheless fully controllable. Collision is one of the major hazards of the sea. To reduce the risks IMO traffic routing schemes are now established in most congested sea areas. Oil tanker companies developed their own voluntary routing system in the Malacca Straits pending the implementation of the IMO scheme. The introduction of automatic radar plotting aids (ARPA) for ships will also assist in reducing the collision risk.

Navigation and communication systems are now enhanced by the use of satellites, and future developments will lead to the use of satellites in a Global Maritime Distress and Safety System.

Repair and Maintenance

The average oil tanker is effective for about 340 days a year. The remaining days are required for routine repair and maintenance, for dealing with random breakdown, and for regular survey. All ocean-going merchant ships are required by the classification societies to be surveyed at four-yearly intervals, although some parts of the machinery and the boilers are surveyed more frequently. Until recently it was the practice to dry-dock ships once every twelve months in order to carry out the necessary maintenance work. However, as ships have become bigger and the techniques of operating them more sophisticated, the periods tend to be stretched. For all vessels the mandatory dry-docking period is two years with a possible six-month extension. The present rules, however, allow for the in-water survey of VLCCs at the $2\frac{1}{2}$-year mark with mandatory dry-docking at the five-year mark. This rules applies for the first ten years of a VLCC's life. Many large companies carry out their own independent structural surveys on a regular basis to monitor any structural deterioration. The four-year cycle remains in force but it can be extended to five years if an examination is carried out by the Classification Society at the fourth year. Voyage repairs between times are carried out with the ship afloat. This is an expensive part of tanker operations and the practice is to adopt a system of Planned Maintenance. The system is a combination of Planned and Condition Monitoring Maintenance. With the modern techniques in vibration analysis up to 50 per cent of maintenance is based on this system. Most societies allow surveys of certain machinery to be carried out at sea by the Chief Engineer, to reduce to an absolute minimum the time when the ship herself has to be taken out of service for overhaul.

COMMERCIAL ASPECTS

Tonnage Requirements

Each major oil company has its own methods of co-ordinating the activities of its shipping organization, but for them all the programming of tankers to provide the most economic and satisfactory service for the parent oil company has been a complex operation. Shipping has had to react to the inevitable changes occurring in the supply and marketing patterns. The past ten years have seen some fundamental changes in the oil supply pattern. Alaskan and North Sea oil have come on stream, the OPEC countries have asserted control of crude oil supply, and overall demand for crude oil in the non-communist world has become stagnant compared with the high rate of growth in the 1960s. This has resulted in more direct oil shipments outside of the oil companies' control and some refinery closures.

Oil companies' tanker requirements have been reduced and their programming methods made less complex. Nevertheless they must make medium and long term estimates of their shipping requirements for both crude oil and products. From these estimates a strategy must be devised for acquiring or chartering the necessary tonnage, taking full account of the overall world tanker market and a projection of probable future supply and demand of tankers. In this age of uncertainty the strategy must be flexible and robust to the most likely outcomes.

It would probably include a mixture of owned, time-chartered, and voyage-charted tonnage, and the proportion would be different for each company as it assessed its needs and how much of that requirement might be a substantive base-load requirement or marginal, uncertain business.

Chartering

Chartering means hiring other people's ships to conduct one's own business and there are three main types of charter; time charter, single-voyage charter, and consecutive voyage charter.

In a time charter the ship is hired for a given period and payment is made monthly in advance at an agreed rate per deadweight ton per month. Under this type of arrangement the hirer arranges the ship's voyage and deals directly with the Master so far as the programme is concerned, although the ship remains under the management of its owners. In a single-voyage charter the ship is hired for the carriage of one cargo, and freight is paid on delivery at an agreed rate per ton of the cargo carried. A consecutive-voyage charter provides for a given number of voyages, or for as many voyages as can be completed within a stipulated period, each voyage following consecutively. Freight is paid similarly to a single-voyage charter.

Petroleum is normally marketed on the basis of long-term contracts so that the shipping requirements of a large major are likely to be dealt with similarly, and such tonnage as it does not own itself is hired on time charter where possible, thus allowing freer use of the ships and more flexibility in programming. Voyage charter market rates tend to fluctuate, but it is convenient to take a proportion of tonnage in this form. Many independent

shipowners prefer voyage charter activity, especially where the market is buoyant. Voyage charter rates are normally expressed and negotiated by reference to standard rate schedules of which the best known is now called Worldscale. The rate is stated as a number, thus W.95 or W.123, with W.100 as the standard. Numbers below 100 indicate low rates and those above 100, high rates. A basic feature of these rates is that built into them is an allowance for a return ballast passage equivalent to the original loaded passage. This puts the hired ship back in position to engage on her next freight earning voyage.

Marine Insurance

Accidents at sea are not infrequent and claims are a regular feature of shipping activity and an important item of cost. Insurance is of two kinds. The first is marine insurance proper covered by policies underwritten by Lloyd's or other underwriters and providing cover against damage received by the ship through grounding, collision, striking jetties and other structures, heavy weather, machinery damage, salvage, fire and explosion, and ice. The second type of insurance is against third party liabilities and is provided by mutual protection and indemnity associations. This covers for cargo claims, loss of life, personal injury, damage to jetties and structures and other property, fines and other minor liabilities. Neither form of insurance covers for loss of use or loss of profit of the insured ship, although if properly included as a Third Party claim these may be recoverable in collision cases.

Ports and Harbours

In the oil trade there are basically two kinds of ports to which tankers trade—those special ports in which the only commodity dealt with is oil and those ports in which an oil installation is located within a general harbour complex. In the first case the installation, jetties, berthing arrangements, and much of the auxiliary equipment and support needed to operate the port are often placed there by the oil company or companies in whose interests they operate. Examples of this type of port are the Kuwait Oil Company's terminal at Mina-al-Ahmadi or the major Iranian oil port at Kharg Island. Milford Haven in Pembrokeshire is an example of a receiving port which is dominated by the oil industry. Examples of the second type of port are legion, from a major port such as Rotterdam with its own oil dock system to much smaller ports in which there may only be one shared jetty for the import of oil products.

With the advent of large, deep-draught ships, the cost of providing piled jetties to accommodate them in deep water and the cost of approach arms to such jetties is prohibitive. In many places, and especially in production areas, offshore berths are commonplace and take several forms. The Conventional Buoy Mooring (CBM) was the original, and consists of a number of buoy moorings to which a ship, moored to two anchors, secures her stern, the berth being fed by submarine pipelines. In less sheltered waters and for the largest ships, a Single Point Mooring (SPM) is likely to be used. This may take the form of a Single Buoy Mooring (SBM) with Catenary Anchor Leg Mooring (CALM) or Single Anchor Leg Mooring (SALM), or a fixed tower structure.

Whether the main structure is a large buoy or tower, the feature common to all SPMs is a central pipe swivel and turntable carrying a mooring arm and the hose or pipe connections. The ship is moored bow on and is free to weathervane around the SPM facility. Usually floating hoses are coupled from the SPM to the amidships manifold of the ship. In the hostile environment of the North Sea and similar locations, where SALMs of various types have been installed, specialized mooring equipment and bow hose or pipe connection systems may be used.

The design of oil ports and jetties or offshore berths to accommodate ships of up to half a million tonnes deadweight is a highly specialized field of civil engineering in which the oil companies themselves play a major role.

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9

Chemistry and Physics of Petroleum

By R. E. BANKS and P. J. KING

INTRODUCTION

PETROLEUM* is natural organic material composed principally of hydrocarbons which occur in the gaseous or liquid state in geological traps; the liquid part, after being freed from dissolved gas, is commonly referred to as *crude oil*.† Underground reservoirs adopt various forms, and the oil is usually associated with natural gas and brines. In a typical dome-shaped formation, the fluids occupying the interstices in the rock are arranged in order of increasing density with ill-defined boundaries between zones. Uppermost is the gas zone or cap which contains so-called associated (i.e. with oil) natural gas; this comprises low-molecular-weight alkanes—methane (predominantly) plus its C_2–C_7 homologues (ethane, propane, butanes, pentanes, hexanes, and heptanes) together with inorganic gases (carbon dioxide, nitrogen, hydrogen sulphide, and sometimes helium). The intermediate zone contains oil saturated with dissolved gas under the conditions of temperature and pressure prevailing in the reservoir rock; and the bottom zone is occupied by 'connate' or 'interstitial' water, traces of which are also present in the pores of reservoir rock in the oil and gas zones. Oilfield waters (or 'brines') contain relatively large amounts (frequently more than 10^4 ppm) of dissolved inorganic salts—principally chlorides and sulphates of sodium, potassium, calcium, and magnesium.

In a producing oilfield, the fluid obtained at the wellhead is subjected to degassing and (if necessary) dehydration operations for removal of gas and any salt water, respectively, from the crude oil prior to its dispatch to the refinery or export point. In the first operation, gases evolved when pressure on the wellhead fluid is released are burned ('flared') or recovered, stripped of their less volatile constituents (butanes and 'pentanes plus'), then either sent to consumer centres as natural gas or used to re-pressurize the oilfield; the liquid constituents are marketed as 'stabilized natural gasoline', suitable for blending with other gasolines. The objective of the second operation is to eliminate water from the crude oil, with which it can form very stable emulsions; clearly, if salt water were left in the oil it would occupy vital space in storage and transport facilities, and it must be removed prior to refining if serious corrosion problems are to be avoided.

The majority of geochemists believe that petroleum originates from buried sedimentary organic matter derived from biopolymers produced by plants and animals (lignin, carbohydrates, lipids, and proteins); diagenesis—biological, physical, and chemical alteration of this organic matter prior to a pronounced effect of heat—leads to complex geopolymers known collectively as kerogen,

* Derived from the Latin words *petra* (rock) and *oleum* (oil).

† Simply termed 'crude' in the petroleum industry.

which is the main organic constituent of ancient sediments. Two main types of kerogen are recognized, a 'coaly' type which does not contribute to petroleum and a 'sapropelic' type which does. Thermal conversion of sapropelic kerogen into oil and gas occurs as the temperature rises during burial of sediments. Once formed in dense fine-grained source rocks, oil and gas undergo primary migration into more permeable coarse-grained sedimentary reservoir rocks where movement (so-called secondary migration) of the fluids within the pores eventually leads to their segregation into accumulations. Oil-bearing formations range in age from the early Palaeozoic era (500×10^6 years) to the late Cenozoic (10^6 years); particularly prolific oilfields belong to the Cenozoic and Mesozoic periods (reaching back 225×10^6 years).

CHARACTERISTICS OF CRUDE OILS

Definition, Appearance, and Composition

One authority defines crude oil or petroleum as follows (ASTM D288): 'A naturally occurring mixture, consisting predominantly of hydrocarbons and/or of sulphur, nitrogen and/or oxygen derivatives of hydrocarbons, which is removed from the earth in a liquid state or is capable of being removed. Crude petroleum is commonly accompanied by varying quantities of extraneous substances such as water, inorganic matter, and gas. The removal of such extraneous substances alone does not change the status of the mixture as crude petroleum. If such removal appreciably affects the composition of the oil mixture, then the resulting product is no longer crude petroleum.'

From the outset, it must be stressed that crude oil is not a uniform substance: its appearance and characteristics vary from oilfield to oilfield, and even from well to well in the same oilfield. Thus each separate accumulation of petroleum is a unique mixture, not matched exactly in composition by any other sample; and it may not even be homogeneous, since it can contain colloidal suspensions besides dissolved gases and solids. Physically, crude oils can vary from light, mobile, straw-coloured liquids containing a large proportion of easily distillable material to highly viscous, semi-solid black substances from which very little material can be removed by distillation before the onset of thermal decomposition. Densities generally lie in the range 0.79 to 0.95 g/cm^3 under surface conditions, and viscosities vary widely, from about 0.7 centipoise to more than 42 000 centipoise. In general, crude oils are flammable under ambient conditions and their odours can vary from an almost pleasant aromatic bouquet to the distinctly unpleasant smell often associated with sulphur derivatives.

Despite the wide differences in the physical aspects of different crude oils, their ultimate or elemental compositions are remarkably consistent; thus, the values of the percentages by weight of the elements present in a 'crude' fall within the narrow limits quoted in Table I. This apparent contradiction was explained at the turn of the century by C. F. Mabery, who, on the basis of the evidence available at that time, postulated that crude oils are mainly composed of hydrocarbons belonging to a few homologous series, with individual members of each type being quite numerous. In this way, the differences between crude oils could be explained by the relative amounts of each series present in a given oil, and the extent to which individual members of a series appear in the crude. This view has been corroborated by modern studies.

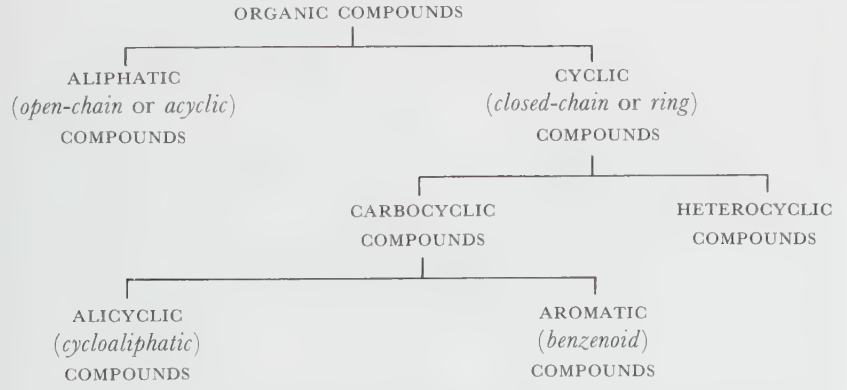
TABLE I
Elemental Composition/wt-% Ranges for Crude Oils

Carbon	83.9–86.8
Hydrogen	11.0–14.0
Sulphur	0.06–8.00
Nitrogen	0.02–1.70
Oxygen	0.08–1.82
Metals*	0.00–0.14

CONSTITUENTS OF CRUDE OILS

As indicated by the analytical data listed in Table I, the main constituents of crude oils are hydrocarbons, i.e. compounds composed solely of hydrogen (H) and carbon (C), and these can account for over 75 per cent of the material. Of the other elements present, sulphur (S), nitrogen (N), and oxygen (O) appear as heteroatoms in hydrocarbon derivatives, some of which occur as petroporphyrins, i.e. complexes involving traces of metals [notably vanadium (V) and nickel (Ni)] present in petroleum.* Metals may also be combined as salts of carboxylic acids, but much remains to be learned about the structural affiliations of metallic and metalloidal elements in crude oil. Inorganic sulphur can be present as the element or as hydrogen sulphide (H_2S) dissolved in the oil. Heavy crudes of the younger formations, for instance Venezuelan crudes, have a low hydrocarbon content of the order of 35 to 38 per cent, the remainder comprising compounds with molecules containing at least one heteroatom. Non-hydrocarbon components are concentrated mainly in the heavy residues (residuum) from the distillation of crudes.

In the discussion which follows immediately, the types of carbon compound (*organic* compound) present in crude oil are defined and exemplified. Readers are reminded that organic compounds may be classified according to the basic scheme set out below. All the classes shown are represented in petroleum.



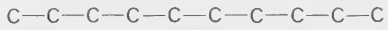
* The most abundant 'trace' metals are vanadium and nickel; numerous others (e.g. iron, magnesium, aluminium, copper, silver) have been detected, but no systematic analytical work seems to have been carried out, and it is difficult to evaluate whether their occurrence is common or not.

Hydrocarbons

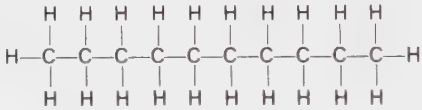
The principal types of hydrocarbon present in crude oils are normal, branched, or cyclic *saturated hydrocarbons, aromatic hydrocarbons,* or compounds with molecular structures associating *both* these basic types. *Unsaturated* hydrocarbons, such as alkenes (aliphatic olefins), appear to be present in only traces—if at all.

Alkanes

Originally and still known as *paraffins,* these are saturated, aliphatic (i.e. open-chain), normal (i.e. straight-chain), or branched (i.e. branched-chain) hydrocarbons which constitute the homologous series of general formula C_nH_{2n+2}. The carbon atoms forming the molecular skeleton of a normal alkane, e.g. n-decane (n-$C_{10}H_{22}$), are connected to one another by single bonds:

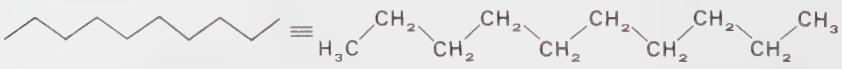


and when the hydrogens are appended (carbon is quadrivalent) the drawing is called an extended structural formula:

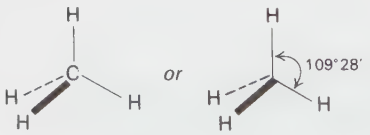


It is much more convenient to use contracted structural formulae, e.g.

and quicker still to draw skeletal or 'stick' formulae in which lines represent C—C, hydrogen substituents are omitted, and C—C—C angles are indicated:



When it is necessary to describe three-dimensional spatial relationships between atoms in a molecule of an alkane (or any other compound), stereoformulae are used in which a line of normal thickness denotes a bond lying in the plane of the paper, a broken line denotes a bond projecting behind the paper, and a thickened line denotes a bond projecting in front of the plane of the paper; this is illustrated below for methane.



All the straight-chain or linear alkanes (n-alkanes) from C_1 (CH_4, methane) to C_{40} ($C_{40}H_{82}$, tetracontane)* and a few beyond have been identified in crude oil; they usually amount to 15 to 20 per cent of the oil, but their content can be quite low, as in heavy degraded oils, or as high as 35 per cent in light crudes ('paraffinic crudes'). High-molecular-weight n-alkanes ($>C_{20}$) are responsible for high cloud points, i.e. temperatures at which a cloud of 'paraffin wax' crystals appears when the oil is chilled.

As one ascends the homologous series of alkanes, it is possible from butane (C_4) onwards for the carbon atoms to be arranged in linear or branched fashion, for example

$$CH_3—CH_2—CH_2—CH_3 \equiv CH_3CH_2CH_2CH_3$$

or

$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3 \equiv (CH_3)_2CHCH_3$$

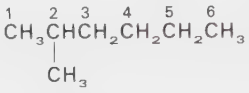
The upper set of formulae belongs to n-butane and the lower to isobutane (*iso*alkanes are branched-chain alkanes in which branching is associated with a single methyl† group on the penultimate carbon atom); these distinct compounds are termed *constitutional isomers*, isomers being compounds which have identical molecular formulae but differ in the nature or sequence of bonding of their atoms or in arrangement of their atoms in space. Clearly, as the number of carbon atoms in an alkane molecule increases, so does the number of possible isomers; thus, for example, there are three isomeric pentanes (C_5H_{12}), 4347 pentadecanes ($C_{15}H_{32}$), and 62 491 178 805 831 tetracontanes ($C_{40}H_{82}$). Isomers possess slightly different physical properties, and their chemical reactions differ in rate not type; hence the general properties of the series are maintained.

Owing to structural isomerism, the number of individual compounds which can be present in a crude oil fraction increases considerably with boiling point (in each hydrocarbon series, the volatilities of members decrease as the number of carbon atoms per molecule increases). Analysis of crude oil fractions has revealed that the predominant members of the branched-chain alkane class are those carrying the simplest type of side-chain, namely methyl, CH_3—. The highest individual concentration of such alkanes is found in the C_6 to C_8 range,

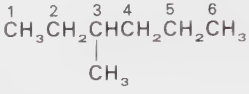
* The first four alkanes have special names (methane, ethane, propane, and butane) related to their histories; from C_5H_{12} (pentane) onwards, Latin or Greek numeral roots are used to reveal the number of carbon atoms per molecule.

† Univalent groups stemming from the removal of one hydrogen atom from an alkane are known as alkyl groups; the name of each group is obtained by changing the suffix *-ane* of the parent hydrocarbon into *-yl*. C_1–C_4 alkyl groups are often represented by the shorthand notations Me, Et, Pr, and Bu respectively; all isoalkanes contain the isopropyl group, $(CH_3)_2CH$ i-Pr. As in the discussion of the mechanisms of reactions involved in refinery processes (p. 299), the symbol *R* is used to represent an unspecified alkyl group.

which contains 2- and 3-methyl-compounds (iso- and anteiso-, respectively), for example



2-methylhexane* (b.p. 90°C)
(isoheptane)



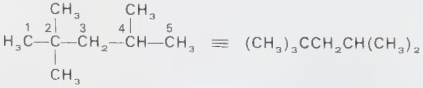
3-methylhexane* (b.p. 92°C)
(anteisoheptane)

Several branched C_{10} alkanes are particularly abundant in crude oils, owing, it has been proposed, to their derivation from monoterpenoids (monoterpenes) of higher plants, for example

limonene† 3-isopropylheptane

Terpenoids are also called isoprenoids because of their structural relationship to head-to-tail addition polymers of isoprene [2-methylbuta-1,3-diene, $CH_2{=}C(CH_3)CH{=}CH_2$]. Branched-chain alkanes [isoprenoid (ip-) hydrocarbons] presumed to be derived from higher terpenes and carrying a methyl group on every fourth carbon atom amount to 1 per cent of crude oil, the most abundant being pristane ($C_{19}H_{40}$, ip-19) and phytane ($C_{20}H_{42}$, ip-20). These 'regular' (structure-wise) acyclic isoprenoids are two of the best known 'biological markers'—a term used to describe oil components whose basic structures (carbon skeletons) relate to compounds frequently found in

* These are IUPAC (International Union of Pure and Applied Chemistry) names, as distinct from the so-called trivial names given in parentheses; the arabic numerals have been placed over the carbons in the chain belonging to the 'parent' alkane to indicate how the positional locants for the methyl substituents are determined. The IUPAC system provides a simple, unequivocal system of nomenclature required for C_6 alkanes upwards (C_5 upwards some would say) which, briefly, involves numbering the longest carbon chain from end to end, the direction being so chosen as to give the lowest numbers possible to the side chain(s). Thus, isoheptane is 2-methylhexane *not* 5-methylhexane. The prefix *neo* in trivial nomenclature is used when a quaternary carbon atom (i.e. one attached to four other carbons) is present, so the three possible isomeric pentanes (C_5H_{12}) are n-pentane ($CH_3CH_2CH_2CH_2CH_3$), isopentane [$(CH_3)_2CHCH_2CH_3$], and neopentane [$(CH_3)_4C$]. Since the prefix *iso* should be used only when the only chain branching present is that caused by the presence of a methyl group attached to the penultimate carbon in a linear skeleton of carbons, use of the incorrect name iso-octane for the highly-branched alkane associated with octane ratings for gasoline is somewhat unfortunate; according to IUPAC rules, it is 2,2,4-trimethylpentane:

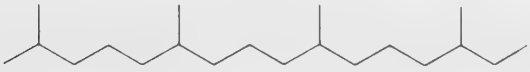


'iso-octane'

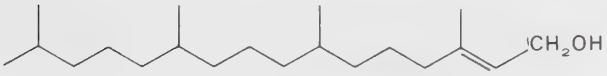
† This is a trivial 'source-based' name.

plant and animal matter; in these cases, a single source is implicated: the acyclic diterpenoid phytol, derived from hydrolysis of chlorophyll.

pristane
(2,6,10,14-tetramethylpentadecane)



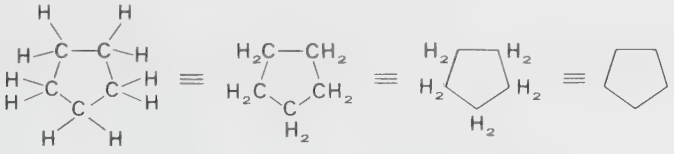
phytane
(2,6,10,14-tetramethylhexadecane)



phytol

Cycloalkanes

Obviously these are cyclic analogues of alkanes. Known formerly as cycloparaffins, and called *naphthenes* in the petroleum industry, these saturated hydrocarbons resemble their aliphatic analogues in many ways—both chemically and physically. They belong to the group of organic compounds known collectively as *carbocyclic* or *homocyclic* compounds, possess the general formula $C_nH_{2n+2-2R_N}$ (R_N = number of naphthenic rings present), and are classified as *alicyclic* (*ali*phatic *cyclic* compounds) to indicate their chemical affiliations with alkanes. The average crude oil contains about 50 per cent by weight of naphthenes, with the quantities increasing in the heavier fractions.* Of the various ways of depicting the structures of cycloalkanes (illustrated below for cyclopentane), the common procedure of representing rings of carbon atoms by idealized polygons is adopted here.

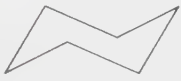


Note that such drawings do not reveal the actual shapes of cycloalkane molecules, i.e. their three-dimensional geometries. Cyclopentane, for example, is not a planar compound but rather is slightly puckered or folded, and cyclohexane prefers to adopt a distinctly non-planar 'chair' conformation in which the ring angles are 111°, i.e. much closer to the tetrahedral value

* They will be more abundant in a middle distillate than in a light distillate for example, but the content will probably decrease in the residual fraction where aromatic and polar compounds predominate.

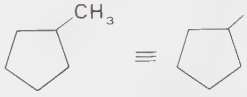
(109° 28′) than the common planar hexagonal formulation (as used below) mistakenly indicates.

envelope conformation of cyclopentane



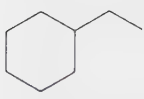
a chair conformation of cyclohexane

The *monocyclic* cycloalkanes cyclopentane and cyclohexane and their alkyl derivatives of low molecular weight ($<C_{10}$) are important constituents of petroleum; commonly the most abundant of these are methylcyclopentane and methylcyclohexane, which together represent 2 per cent or more of the average crude. Compounds containing higher alkyl groups than methyl or more than one alkyl substituent are exemplified below. Members of this sub-class ($R_N = 1$, therefore general formula = C_nH_{2n}) possessing rings smaller than C_5 or larger than C_6 appear to be uncommon constituents of petroleum.

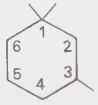


methylcyclopentane

methylcyclohexane



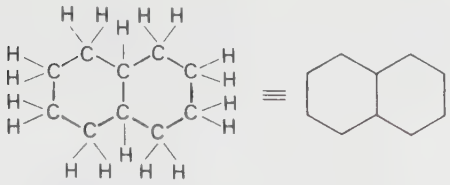
ethylcyclohexane



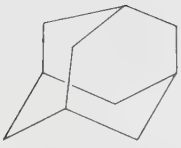
1,1,3-trimethylcyclohexane

The naphthenes present in the heavier fractions tend to be of the *fused* polycyclic type, i.e. two rings share two adjacent carbon atoms. Examples are the bicyclic C_{10} compound decalin ($R_N = 2$; $C_{10}H_{18}$) and the C_{27} tetracyclic hydrocarbon cholestane ($R_N = 4$; $C_{27}H_{48}$). Bicyclic naphthenes are important constituents of the kerosine and gas-oil fractions. Tetracyclic and pentacyclic compounds average >25 per cent of the total $>C_{10}$ naphthenes; their structures are closely related to naturally-occurring tetracyclic steroids and pentacyclic triterpenoids, respectively, and they appear in lubricating oil fractions, causing them to display optical activity.* Hydrocarbons of the adamantane series are also present in crude oils, where they may amount to 10 to 15 per cent of the tricycloalkanes present. Adamantane—a tricyclodecane ($R_N = 3$; $C_{10}H_{16}$) is an example of a *bridged* polycyclic, i.e. the rings share non-adjacent carbons.

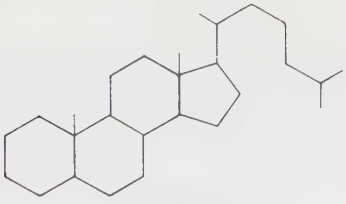
* That is, they possess the ability to rotate the plane of plane-polarized light.



decalin or decahydronaphthalene
(a bicyclodecane)



adamantane*
(a tricyclodecane)



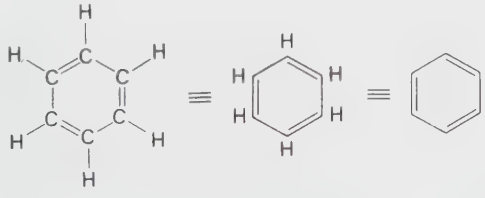
cholestane
(a tetracycloheptacosane)

Alkenes and Cycloalkenes

These are *olefins*, i.e. hydrocarbons containing a carbon–carbon double bond, C=C. Reports on the isolation and identification of compounds of this class from petroleum seem rare. C_6 to C_8 alkenes, for example oct-2-ene, $CH_3CH{=}CHCH_2CH_2CH_2CH_2CH_3$, present to the extent of at least 0.6 per cent by volume in the gasoline fraction of Bradford crude oil (a typical Pennsylvania crude) were investigated more than thirty years ago; more recent work has involved studies on polycyclic cycloalkenes present in certain young crudes.

Arenes

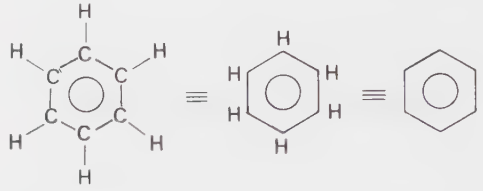
Called *aromatics* (short for aromatic hydrocarbons) in the petroleum industry, arenes are carbocyclic compounds of the *benzenoid class*, the archetype of which is the monocyclic compound benzene, C_6H_6. The structure of this parent compound can be represented either by means of a so-called Kekulé formula:



or a Robinson–Armit 'picture' in which the circle in the ring symbolizes the view that six π-electrons in the symmetrical planar benzene molecule produce a

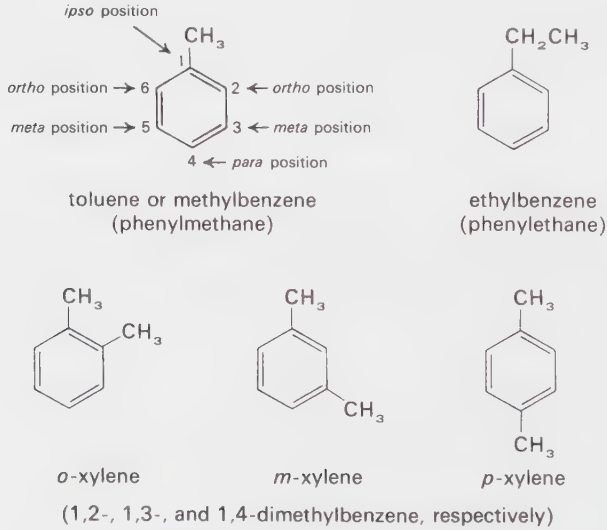
* Note that all three cyclohexane units are constrained in chair conformations.

stable configuration which is responsible for the *aromatic character* (chemical and physical) of the substance:



Kekulé structures are used here to represent benzene and related aromatic molecules, and the reader is reminded that in each case only one of a set of canonical forms is shown. Benzene, of course, is a resonance hybrid, the major canonical forms (contributing structures) being two completely equivalent Kekulé structures:

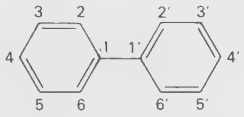
In addition to benzene and its homologues [alkyl derivatives, e.g. toluene,† ethylbenzene, and *ortho-*, *meta-*, and *para*-xylene†—which are sometimes classed as aralkanes (*arylalkanes*)*] crude oil contains *polynuclear* aromatic hydro-



* An aryl group is the class name for a univalent aromatic group derived by the conceptual removal of a hydrogen from a carbon of an aromatic nucleus, i.e. from a ring carbon. The simplest aryl group is phenyl, C_6H_5—, derived from benzene(phene) itself.

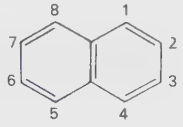
† Such common or trivial names abound in aromatic chemistry.

carbons of two types—*isolated* (or *non-condensed*), e.g. biphenyl, and *condensed*, e.g. naphthalene, plus their homologues.

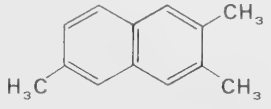


biphenyl*

Condensed polynuclear systems take various forms, depending on the number of benzene nuclei fused together and the modes of fusion (*ortho* or *ortho* plus *peri*). In naphthalene and its homologues for example, two benzene nuclei are *ortho*-fused (or cata-condensed), i.e. two benzene rings share two vicinal (adjacent) carbon atoms.

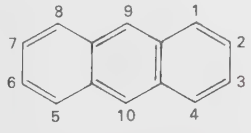


naphthalene

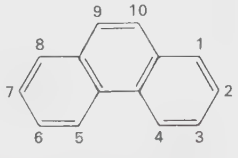


2,3,6-trimethylnaphthalene

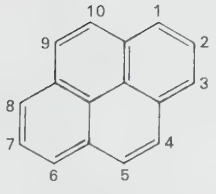
Alkylanthracene and alkylphenanthrene components of oils are derived from the trinuclear aromatics exhibiting the two possible modes of *ortho*-fusion (cata-condensation) of a benzene nucleus to naphthalene, namely *linear* and *angular* (or non-linear). Linearly, cata-condensed compounds are called *polycyclic acenes*, and their bent or angular analogues *polycyclic phenes*. Pyrene is an example of an *ortho*- and *peri*-fused polynuclear aromatic constituent of crude oils; its non-linear *ortho*-fused analogues benz[*a*]anthracene and chrysene are also known components.



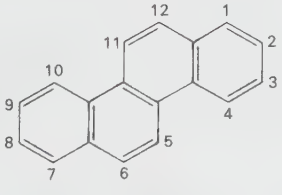
anthracene
(a *linear* polynuclear aromatic)



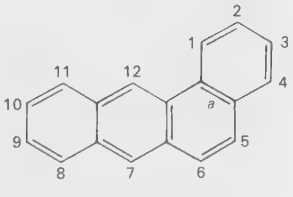
phenanthrene
(an *angular* polynuclear aromatic)



pyrene
(*ortho*- and *peri*-fused)



chrysene
(*ortho*-fused)

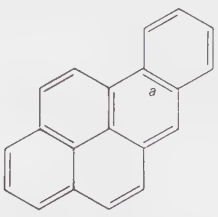


benz[*a*]anthracene
(*ortho*-fused)

* Phenyl, C_6H_5—, is the *aryl* group derived from the conceptual removal of hydrogen from benzene (phene).

Aromatic hydrocarbons do not normally amount to more than 15 per cent by weight of a total crude oil; the mononuclear compounds toluene and *m*-xylene are the most common arenes found, and polynuclear species containing up to at least eight condensed rings seem to be possible constituents. Compounds belonging to all the basic types defined above have been found in crude: benzene (one ring); naphthalene (two rings); anthracene and phenanthrene (three rings); and pyrene, benzanthracene, and chrysene (four rings). The most abundant of these components possess benzene, naphthalene, and phenanthrene ring systems, with alkyl derivatives containing one to three additional carbon atoms being more prevalent than the parent compounds; for example, while benzene normally comprises up to only 1 per cent by weight of crude oil, toluene and xylene (three isomers—see p. 288) concentrations may reach 1.8 per cent and 1.3 per cent, respectively. The heavy gas oil, lubricating oil, and residuum of petroleum contain increasing amounts of polycyclic aromatics, and those appear to be predominantly *ortho*-fused systems. Methods of Structural Group Analysis (see p. 318) are based on this assumption. The general formula of *ortho*-condensed aromatics is $C_nH_{2n+2-6R_A-2R_{AS}}$, where R_A is the number of aromatic rings and R_{AS} is the number of 'substantial aromatic rings', i.e. the first benzene ring in an *ortho*-fused group.

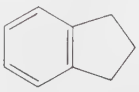
A number of the polycyclic aromatic hydrocarbons present in petroleum are carcinogens, the best known being the strongly-active compound benzo[*a*]-pyrene. King has recently assessed the potential carcinogenic hazard of petroleum hydrocarbons (see the Bibliography).



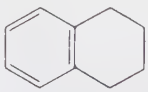
benzo[*a*]pyrene

Cycloalkanoarenes

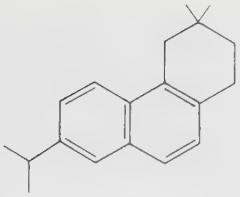
These 'mixed' polycyclic hydrocarbons, referred to as *naphthenoaromatics* by petroleum chemists, possess structures involving fusion of aromatic with alicyclic rings, and may, of course, carry aliphatic side-chains; when they do, they contain all three types of C/H molecular 'building block' discussed so far. As a class they begin to appear in the kerosine fraction, increasing in concentration in the higher-boiling distillation cuts and residues. Examples of compounds present are given below.



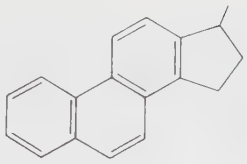
indane
(C_9H_{10})



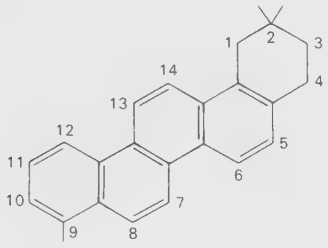
1,2,3,4-tetrahydronaphthalene
(tetralin; $C_{10}H_{12}$)



7-isopropyl-3,3-dimethyl-1,2,3,4-tetrahydrophenanthrene ($C_{19}H_{24}$)



3'-methyl-1,2-cyclopentenophenanthrene ($C_{18}H_{16}$)



2,2,9-trimethyl-1,2,3,4-tetrahydropicene ($C_{25}H_{24}$)

Examination of several crude oils has shown that bicyclic naphtheno-aromatics (one aromatic ring and one alicyclic)—indane, tetralin, and their alkyl derivatives—are relatively abundant in kerosine and light gas oils. The tricyclic compound 1,2,3,4-tetrahydrophenanthrene and its derivatives are also common. Of particular importance to studies on the origin of oil is the presence in heavier gas oils or lubricating oil fractions of tetra- and pentacyclic naphtheno-aromatics related to steroid and triterpenoid structures.

Non-hydrocarbons

Crude oils contain appreciable amounts of organic compounds with structures incorporating one or more (the same or different) atoms of sulphur, nitrogen, or oxygen in addition to carbon and hydrogen; and some of these are associated with metals such as vanadium and nickel, i.e. they are organometallic in nature. As a class, these organic non-hydrocarbon components are distributed throughout the whole boiling range of a crude oil, but appear mainly in the heavier distillation fractions and the non-volatile residue. Although concentrations of non-hydrocarbons in any one fraction may be relatively small, their influence can be important; for example, acidic components such as thiols and carboxylic acids promote corrosion of metal equipment; reforming catalysts employed in the production of motor gasoline are seriously deactivated by sulphur compounds; trace metals (V, Ni) become deposited on and passivate and/or poison catalysts employed in desulphurization of fuel oil or catalytic cracking of heavy distillates. Clearly, knowledge of the presence and characteristics of these non-hydrocarbons is important to the petroleum technologist. Geochemists also are keenly interested in this class of crude oil component from the viewpoints of the elucidation of the origin of petroleum (of

particular interest is the source of *petroleum porphyrins*, complex organometallic compounds containing porphin skeletons and related to chlorophyll or haemin) and of the mechanisms of its migration from source to reservoir rocks (discussion here centres on surfactant properties of polar N-, S-, and O-containing components). The colour and odour of crude oil stems mainly from the NSO compounds that are concentrated in the lubricating oil (C_{26}–C_{40}) and residuum ($>C_{40}$; asphaltic bitumen) fractions.

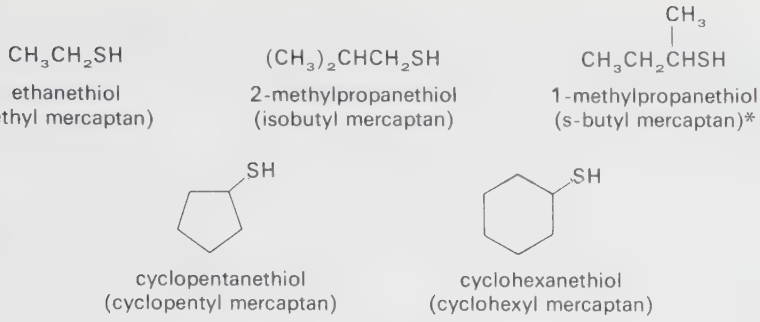
Crude oil may also contain relatively minor amounts of suspended inorganic salts (mainly chlorides—see p. 279) and of dissolved elemental sulphur and hydrogen sulphide. As mentioned previously (p. 279), arrangements are normally made at the wellhead to remove hydrogen sulphide (along with light hydrocarbon gases) and 'salt' associated with oil accumulations. Even small quantities of salt remaining in crude or picked up during shipping can lead to serious problems in the refinery owing to its deposition in distillation plants or conversion there into corrosive acids; its concentration is best reduced, therefore, to less than 0.001 wt-% by washing crude with water at *ca.* 120°C under pressure before distilling it.

Organosulphur Compounds

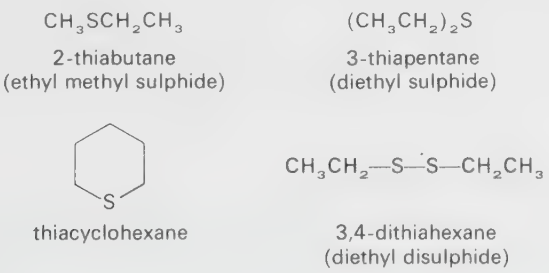
Sulphur is the third most abundant atomic constituent of crude oils, following carbon and hydrogen. Organic derivatives of sulphur are present in all known crudes, although their concentration can vary between wide limits: from <0.05 per cent by weight in some Pennsylvanian oils to 7.9 per cent in Wafra crude. The average sulphur content of crude oils, based on analysis of 9347 samples by the US Bureau of Mines and IFP, is 0.65 per cent by weight; the majority (*ca.* 7500) of the samples examined were 'low-sulphur' crudes (<1 per cent S). Combined sulphur is present in medium as well as heavy fractions of crude oils; sulphur content is not specifically related to the heaviest fractions, as is the case for nitrogen. In the low- and medium-molecular-weight range (up to C_{25}), it is associated only with carbon and hydrogen; in heavier fractions, it is frequently found in polycyclic molecules also containing nitrogen and oxygen (NSO compounds). Since sulphur is not a major constituent of biogenic molecules, where it ranks well behind oxygen and nitrogen, it seems that it must become incorporated into organic structures *en route* from biological source material to petroleum or while crude oil stands in reservoirs. Sulphur isotope measurements have led to the conclusion that a large proportion of the organosulphur compounds present in mature Palaeozoic crudes from Wyoming contain sulphur derived from sulphate ion in connate water after the oil had accumulated. Laboratory experiments support the proposal that the reactions envisaged—oxidation, sulphurization, and dehydrogenation (including aromatization) of hydrocarbons via reactions involving sulphate ion, elemental sulphur, polysulphides, and hydrogen sulphide—could occur under reservoir conditions.*

The organosulphur compounds present in light and medium fractions of crude oil can be divided into three classes: *thiols*, *sulphides*, and *thiophens*.

* For details, see the texts by J. M. Hunt and B. P. Tissot and D. H. Welte listed in the Bibliography at the end of this chapter.



Thiols (originally and still sometimes called *mercaptans*†) are vile-smelling sulphur analogues of the alcohols (i.e. thioalcohols) and characterized therefore by the presence of the sulph-hydryl group, —SH, which takes the place of a hydrogen atom in an alkane or cycloalkane molecule [$RH \rightarrow RSH$ ($RH = C_nH_{2n+2}$ or C_nH_{2n})]. Also viewable as mono-alkyl or mono-cycloalkyl derivatives of hydrogen sulphide ($HSH \rightarrow RSH$), thiols (C_1–C_8) are the principal organosulphur components of low-boiling petroleum fractions (below 200°C), both acyclic (normal and branched) and cyclic compounds being found (examples are given above); ethanethiol is the most abundant compound of this class in Wasson (Texas) crude, amounting to 0.0053 per cent by weight of the total oil. Thiols are stronger acids than alcohols, and use is made of this to remove low-molecular-weight thiols from light gasolines with caustic soda solution. Hydroprocessing techniques are employed to desulphurize other oil fractions, and here combined sulphur is eliminated as hydrogen sulphide from all types of compound containing this heteroatom. In the cases of thiols and monosulphides, the reactions proceed as follows: $RSH + H_2$-catalyst $\rightarrow RH + H_2S$; $RSR' + 2H_2$-catalyst $\rightarrow RH + R'H + H_2S$.

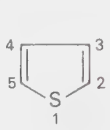


Monosulphides (thia-alkanes and thia-cycloalkanes *or* thio-ethers), i.e. compounds formally derived by replacement of both hydrogens of hydrogen sulphide by hydrocarbon groups (examples are given above) appear in very

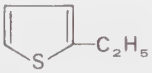
* The s (short for *secondary*) reveals that the —SH group is attached to a secondary carbon atom and not a *primary* one. It is often convenient to designate carbon atoms as primary (1°), secondary (2°), tertiary (3°), or quaternary (4°), depending whether they are bonded to one, two, three, or four other carbons.

† Derived from the Latin words *mercurium* (mercury) and *captans* (seizing), since they react readily with mercuric salts, yielding mercaptides, $(C_nH_{2n+1}S)_2Hg$.

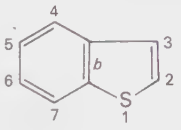
low abundance in crudes (Wasson crude contains 0.0022 per cent of 2-thiabutane and up to 0.0025 per cent of thiacyclopentanes); a few low-molecular-weight *disulphide* analogues of the dialkyl sulphides (dithiabutanes to dithiahexanes, e.g. 3,4-dithiahexane) have also been shown to be present in crudes.



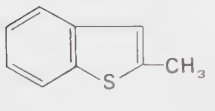
thiophen



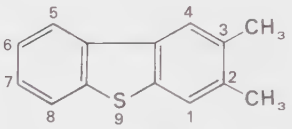
2-ethylthiophen



benzo[*b*]thiophen



2-methylbenzo[*b*]thiophen



2,3-dimethyldibenzothiophen

The third class of organosulphur components of crude oil is characterized by the presence of a *thiophen* nucleus; this may carry one or more alkyl substituents or be fused to one or more other ring systems (aromatic or naphthenic), which can also carry alkyl groups. Some examples of compounds found in crudes are shown above. Thiophen itself, a well-known heteroaromatic (*hetero*cyclic *aromatic*) compound,* and its alkyl derivatives are normally relatively scarce constituents of crudes, but condensed systems—benzothiophens, dibenzothiophens, and higher polycyclics (e.g. benzonaphthothiophens)—are important components of all high-sulphur crudes. Wasson (Texas) crude contains 0.0025 per cent of 2-methylbenzothiophen.

Parent compounds are generally less abundant than their alkyl derivatives, which usually contribute a maximum of two or three additional carbon atoms, principally in the form of methyl groups. Thiophen derivatives are particularly abundant in crude oils containing high proportions of aromatics, resins, and asphaltenes.

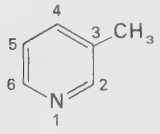
Organonitrogen Compounds

The nitrogen content of crude oils is usually much lower than the sulphur content, and 90 per cent of crudes contain less than 0.2 per cent N by weight; the average value for crudes is 0.094 per cent. In the lighter fractions up to the kerosine range, organonitrogen compounds are present only in traces; their concentration increases with increasing boiling point and reaches a maximum in asphaltic distillation residues [e.g. boiling range/°C and N/wt-% values for Wilmington crude (California) are: up to 130, 0.00; 130–250, 0.0027; 250–300, 0.028; 300–350, 0.10; 350–400, 0.25; 400–500, 0.48; residuum, 0.97]. Unlike some sulphur compounds, the organonitrogen constituents are relatively stable

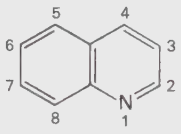
* Like benzene (see p. 287), thiophen is a planar monocyclic system containing $(4n + 2)$ π-electrons ($n = 1$; the sulphur provides two electrons) and so possesses 'aromatic' properties.

towards heat and do not decompose under refinery conditions; their presence in trace amounts in distillates can, however, pose problems.

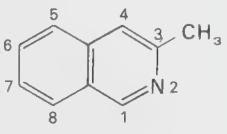
The main part of the nitrogen occurs in high-molecular-weight polycyclic structures, often incorporating other heteroatoms (O, S). Low-to-medium molecular weight compounds of well-defined structures have been isolated from gas oils: about 25 to 30 per cent of these usually consist of the basic (i.e. extractable with dilute mineral acids) *N*-heteroaromatics pyridine, quinoline, and isoquinoline or alkyl (mainly methyl) derivatives thereof, while the rest are relatively non-basic compounds containing the pyrrole nucleus, e.g. indole, carbazole, and methylated analogues.



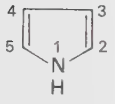
3-methylpyridine



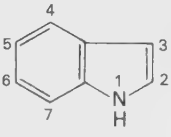
quinoline



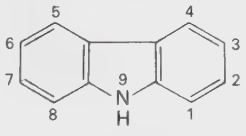
3-methylisoquinoline



pyrrole

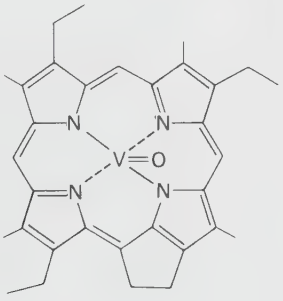


indole



carbazole

The pyrrole nucleus also features in the porphyrin components (free and complexed with metals) of crude oils, the basic porphin skeleton present comprising four pyrrole residues linked by methine (—CH=) bridges; this system forms stable complexes with certain metals, hence the occurrence in



crude oils of metalloporphyrins containing nickel or vanadium (as vanadyl and exemplified above). These so-called petroporphyrins have been studied extensively. They are associated with highly asphaltic crudes, and are active poisons for catalysts used in refinery cracking processes (see p. 304); their structures are closely connected with those of chlorophyll and haemoglobin; hence they are 'biological markers' and provide powerful evidence in support of a biogenic origin of petroleum.

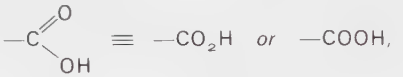
Oxygen-containing Compounds

The commercially-important acidic components of petroleum commonly termed *naphthenic acids* belong to this group.

The total amount of combined oxygen in crude oils is relatively low, varying from traces to a maximum of 2 per cent by weight. The determination of oxygen is difficult, and in many of the early reported analyses oxygen was determined by difference, giving figures which are probably too high. More recent direct determinations of oxygen may also be too high, since at least part of the oxygen so determined may be due to oxidation of the crude oil after removal from reservoirs. The oxygen content increases with the boiling point of the fraction, the greater portion of oxygen-containing constituents being concentrated in the residual oils, where values as high as 8 per cent have been recorded.

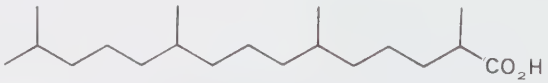
In the low- and medium-boiling range distillate fractions, oxygen is mainly present in the form of carboxylic acids and, to a limited extent, phenols. For this reason the determination of total oxygen content is customarily replaced by a determination of acidity of the fraction. In general, paraffinic crudes and their distillate fractions are low in acidity, whereas asphaltic crudes (i.e. Californian, Venezuelan, Roumanian) frequently contain substantial amounts of acids, of the order of 0.6 to 1.0 per cent by weight or higher. For a given crude, the acidity usually reaches a maximum in the kerosine–gas oil range, while straight-run gasolines, heavy fractions and residues contain only traces of acidic compounds.

Carboxylic acids are very common organic acids characterized by the presence of the carboxyl group, i.e.



$\equiv -CO_2H$ *or* $-COOH$,

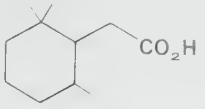
attached to carbon; these can be neutralized with bases to give salts, for example CH_3CO_2H (acetic or ethanoic acid) + $NaOH \rightarrow CH_3CO_2^-Na^+$ (sodium acetate or ethanoate) + H_2O. The identities of carboxylic acids present in crude oil have been the subject of investigations for more than a century, one incentive being provided by the proposal that they may be the precursors of petroleum hydrocarbons. Progress has been slow owing to the enormous complexity of crude oil and the vast number of acids present, hence the massive attendant problem of isolation, separation, and identification of specific groups of components. Thus, with the exception of fatty acids (long-chain alkanecarboxylic or alkanoic acids), the C_{10} limit was not exceeded until the 1960s, when Cason's group, working with middle distillates of a Californian naphthenic-type crude, isolated several (C_{11}, C_{14}, C_{15}, C_{19}, and C_{20}) acyclic isoprenoid* acids, for example



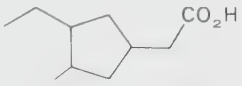
2,6,10,14-tetramethylpentadecanoic acid

* See p. 284 for a definition.

a monocyclic C_{11} isoprenoid acid, namely the *trans*-isomer of 2,2,6-trimethylcyclohexylacetic acid, and geometric isomers of the monocyclic non-isoprenoid C_{10} acid 3-ethyl-4-methylcyclopentylacetic acid. Much more information became available in the early 1970s, when the conventional view

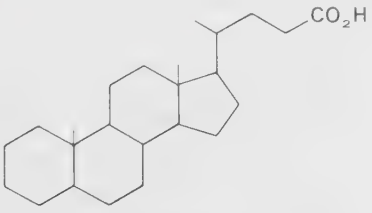


2,2,6-trimethylcyclohexylacetic acid



3-ethyl-4-methylcyclopentylacetic acid

of naphthenic acids as primarily mononaphthenic (i.e. monocycloalkanoic) and alkanoic was expanded by about 40 classes (including polycyclic *N*-, *S*- and *O*-heteroaromatic acids) through reports on work by Seifert and Teeter, who also discovered the presence of steroidal carboxylic acids in petroleum, for example



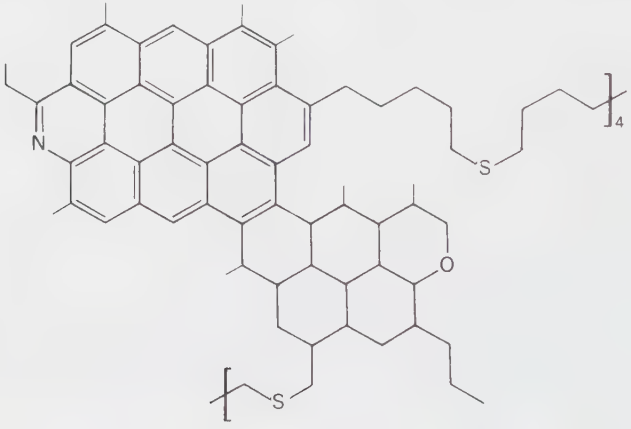
cholanic acid

From an industrial viewpoint (Sisco *et al.*), naphthenic acids have been defined as follows: 'The carboxylic acids that are derived from petroleum during the refining of the various distilled fractions and are predominately monocarboxylic acids. The main distinguishing structural feature of naphthenic acids is a hydrocarbon chain consisting of single or fused cyclopentane rings, which are alkylated in various positions with short aliphatic groups. Other acids, for example aliphatic, dicarboxylic, and those containing the cyclohexane ring, are also present in moderate quantities.' Naphthenic acids are recovered as byproducts from the refining of straight-run petroleum distillates, the majority of the commercial products being derived from kerosine and gas-oil fractions, with some higher-molecular-weight material coming from the light lubricating oil cuts. Separation of the naphthenic acids involves extraction of the oil fractions with caustic soda.

After extraction of the naphthenic acids as sodium salts ('soaps') with dilute caustic soda solution (which also extracts phenols and thiols), the soap stock is acidified with sulphuric acid to regenerate the acids. These are purified by vacuum distillation before conversion into metallic and related naphthenate salts which find widespread industrial use as varnish and paint 'driers' (manganese, cobalt, lead, zinc, and calcium naphthenates), fungicides and wood preservatives (copper and zinc naphthenates), lubricating oil additives (lead naphthenate), corrosion inhibitors for ferrous metals (amine salts), catalysts for free-radical processes (cobalt naphthenate), and gelling agents—as in napalm (aluminium naphthenate).

Very-High-Molecular-Weight NSO-Compounds

These are present in the asphaltic residuum which remains after removal of distillable material from crude oil, and are referred to as *resins* and *asphaltenes*. The residuum mainly comprises very heavy oils, resins, asphaltenes, and high-molecular-weight waxes; addition of liquid propane at temperatures below 21 °C causes the resins and asphaltenes to precipitate, and these can then be separated by dissolving the resins in n-pentane. The asphaltenes are dark brown-black amorphous solids, and the resins may be light- to dark-coloured thick fluids or amorphous solids; resins always seem to be more abundant than asphaltenes, and their ratio varies considerably depending on the crude oil source [e.g. wt-% abundances for resins (R) and asphaltenes (A) in Ellenburger (W. Texas), Wilmington (California), Khaudag (USSR), and Boscan (Venezuela) are: 4.2 R, 0.24 A; 14 R, 5 A; 33 R, 8 A; and 29 R, 18 A, respectively]. About half of the total combined nitrogen and sulphur present in crude oil appears in the form of resins and asphaltenes, most of these elements being present in the form of heterocyclic groups; the probability of all molecular species present containing one or more heteroatoms (N, S, or O) is high. Structural types which contribute to resins and asphaltenes have been deduced through combined nuclear magnetic resonance and X-ray studies. Asphaltene molecules probably consist of sheets comprising some 10 to 20 *peri*-condensed aromatic rings carrying naphthenic and paraffinic (some long-chain) groups; these form aggregates (micelles, MW > 30 000; particles, MW ~ 3000 to 10 000), and are also capable of complexing metals, particularly vanadium and nickel. Resins possess lower molecular weights (500 to 1200) than asphaltenes, and are generally less aromatic in nature and comprise fewer condensed rings. A hypothetical structure for an asphaltene molecule is presented below; the positions of all substituents are quite arbitrary.



Organometallic Compounds

Numerous 'trace' elements have been detected in crude oils besides nitrogen, oxygen, and sulphur—which is only to be expected when one considers the history of petroleum from origin to wellhead. Of the many metals listed (aluminium, barium, calcium, chromium, copper, gold, iron, lead, mag-

nesium, manganese, nickel, silver, titanium, vanadium, etc.), nickel and vanadium are the most abundant and, in the form of petroporphyrins and related complexes (see pp. 281, 295) and structures yet to be identified, appear to be present in all crudes. Their concentrations vary from source to source, total amounts ranging from <1 ppm to in excess of 1300 ppm; Boscan (Venezuela) crude, for example, contains 150 ppm of nickel and 1200 ppm of vanadium. Average abundances, determined by analysis of 64 crude oils from various parts of the world (Australia, Canada, Middle East, North and West Africa, USA, USSR, and Venezuela) are nickel 18 ppm and vanadium 63 ppm, and a good correlation exists between sulphur, asphaltene, and metals content. Systematic analysis of crudes for other metals (and metalloids or non-metals like arsenic, phosphorus, and silicon) does not appear to have been carried out, and much remains to be learned about structural affiliations between the organic constituents of crudes and metals present. Note that some metals, particularly iron, may be derived from pipework, etc. used to extract and transport oil; other sources of inorganic material are finely-divided clays and related mineral matter taken from reservoir rocks along with crude, and—of course—petroleum brines (see p. 279).

REACTIONS OF ALKANES AND CYCLOALKANES; OIL REFINERY PROCESSES AND ETHYLENE PRODUCTION

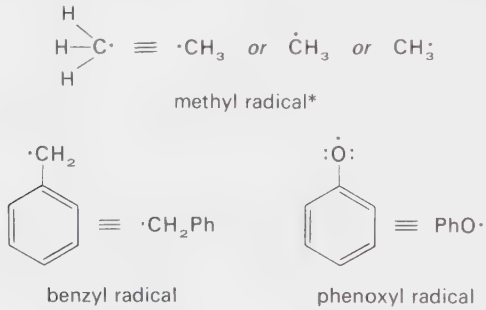
Crude oil is converted into saleable products by a combination of physical (principally distillation) and chemical processes collectively known as *refining*, the prime objective of which is to provide mankind with fuels of correct quality in sufficient abundance. In the early days of the petroleum industry, crude oil was separated by distillation into directly marketable cuts or fractions, often referred to as 'straight run', the compositions and relative proportions of which were dictated by the characteristics of the particular crude being worked. If the refining of crude oil were still confined simply to distillation or other physical methods of separation, which do not markedly affect the chemical composition of a crude, the production of straight-run ('natural') gasoline (boiling range 30–190 °C) would not meet current requirements world-wide, and the octane rating would be inadequate. Several chemical operations—*cracking*, *reforming*, *alkylation*, *polymerization*, and *isomerization*—are mounted at refineries to deal with this problem, and the main task in this section of the chapter is to illustrate the chemical transformation undergone by petroleum hydrocarbons during these operations and during the production of ethylene (ethene), the simplest olefin (alkene) and the cornerstone of the petrochemical industry. For information on the chemistry of *petrochemical processes* used by the chemical industry to convert oil-based raw materials (*primary petrochemicals*) such as ethylene, propylene, benzene, and toluene into the vast array of organic commodities required by our industrial society, the reader should consult (initially) books by Teddar, Nechvatal and Jubb, Wiseman, and Kniel, Winter and Stork (see the Bibliography, p. 327).

Cracking

Several processes used in petroleum refining are based on thermal reactions of hydrocarbons in which the conditions (temperature, pressure, presence of

catalyst, etc.) are chosen according to the end-products desired and feedstock character. In petroleum technology, the term *cracking* is used to describe change in composition of petroleum fractions brought about by the action of heat alone (*thermal* cracking) or heat in the presence of a catalyst (*catalytic* cracking). Cracking, as the word implies, involves decomposition of hydrocarbon molecules via rupture of C—C bonds. Inevitably, the primary products possess lower molecular weights than the feedstocks and are mainly olefinic in nature; secondary products arise via isomerization, cyclization, polymerization, etc., of primary products *in situ* and lead to the production of hydrocarbons both in the same molecular weight ranges as feedstocks and in higher ranges. *Hydrocracking* involves a combination of cracking and hydrogenation.

Note carefully that a fundamental difference exists between cracking promoted by heat alone (thermal cracking) and cracking promoted by heat plus catalysts (catalytic cracking): the former proceeds via a *radical mechanism* (reaction pathway) and the latter principally via a *carbocation mechanism.*



A *radical*† (or *free radical*) is an uncharged species possessing as unpaired electron. Clearly, this definition is very broad since it includes entities such as chlorine or bromine atom (Cl·, Br·), nitric oxide (NO), free methyl, benzyl, or phenoxyl, and paramagnetic metal ions; however, the last type are not normally regarded as radicals. Naturally, the discussion of radicals here is restricted to carbon-centred‡ radicals—alkyl and cycloalkyl—generated initially by thermal C—C bond *homolysis*, i.e. cleavage of a single (two-electron) bond, leaving one of the electrons on each of the fragments. The order of stability of alkyl radicals is $3^\circ > 2^\circ > 1^\circ >$ methyl, e.g. $(CH_3)_3C\cdot > (CH_3)_2CH\cdot > CH_3CH_2\cdot > CH_3\cdot$.

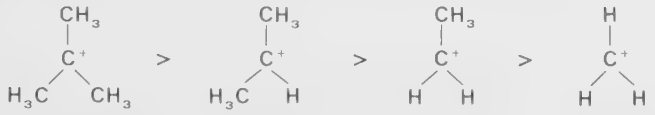
The acid-catalysed hydrocarbon conversions discussed in this section proceed via highly reactive, positively charged species (*reactive intermediates*) which are referred to variously as *carbonium ions*, *carbocations*, or *carbenium ions*.

* If at all possible, the dot symbolizing the unpaired ('odd') electron should be placed so as to indicate precisely the atom of highest spin density. Many authors do not follow this convention and, for example, write methyl radical as shown at the extreme right above.

† The term radical originally denoted a group of atoms which remains intact through a series of reactions, e.g. methyl, isopropyl, phenyl; these are now referred to as *groups* (see footnotes on pp. 283, 288).

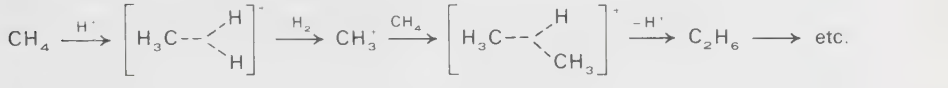
‡ As distinct for example, from oxygen-centred (like phenoxyl) or nitrogen-centred (like $Ph_2N\cdot$) radicals.

Carbocation (*carbon cation*) is an all-embracing term applicable to any cation with an even number of electrons in which the positive charge may be formally localized on one or more carbons; two simple examples are the t-butyl cation, $(CH_3)_3C^+$, and protonated acetone, $(CH_3)_2\overset{+}{C}—OH$. In the past—and some authors still adhere to this practice—*carbonium ion* was used as a generic term for carbocations. The objection to calling trivalent ('classical') ions of the type CH_3^+ carbonium ions is that 'onium ion traditionally implies that a charged atom in an expanded valence state is present, as in tetramethylammonium chloride, $(CH_3)_4N^+Cl^-$; thus, it was argued by Olah, the term carbonium ion should be reserved for hypervalent (e.g. CH_5^+, protonated methane; cf. NH_4^+) 'non-classical' carbocations (real or hypothetical), while the more familiar trivalent 'classical' cations should be called carbenium ions, which implies that they are protonated carbenes (e.g. $H_2C: + H^+ \rightarrow H_3C^+$).* This practice has been widely adopted in recent years. Trivalent alkyl carbocations (carbenium ions) are highly-reactive electron-deficient entities, the *relative* stabilities of which follow the order tertiary > secondary > primary > methyl. For example,



t-butyl cation (3°) | isopropyl cation (2°) | ethyl cation (1°) | methyl cation

Pentavalent carbocations, like methanium ion, are invoked to explain, for example, the polycondensation of methane in the presence of the 'superacid' system $HSO_3F—SbF_5$:



Thermal Cracking

This type of procedure was first commercialized in 1912 to increase the yield of middle distillate fractions (boiling range 150–350°C) from crude oil. Other non-catalytic pyrolytic processes developed include visbreaking, which involves limited molecular degradation of feedstock under mild cracking conditions to improve the viscosity of heavy distillate fractions (>250°C), and coking processes under conditions so severe that feedstock is completely converted into gaseous products, gasoline (boiling range 30–190°C), middle distillate, and coke. Gasoline obtainable by such means is unsuitable for modern internal combustion engines, hence thermal cracking as a petroleum refining process has been replaced by catalytic cracking and hydrocracking.

* Carbene, $H_2C:$, is the prototype of the class of uncharged reactive intermediates containing a divalent carbon atom and two non-bonding electrons. Carbenes ($R_2C:$), carbon-centred free radicals ($R_2C^{\bullet}$), trivalent carbocations (R_3C^+; carbenium ions), and carbanions ($R_3C:^-$) are the four most familiar reactive intermediates in the organic chemist's repertoire.

Thermal cracking is indispensable, however, as a source of primary petrochemicals, notably ethylene (ethene), $CH_2{=}CH_2$. In the US, most of the ethylene is obtained via pyrolysis of ethane from natural gas; in most other developed countries, straight-run naphthas and gas oils are the usual feedstocks in the so-called 'steam cracking' process.

Typically, 'full range' naphtha, boiling range *ca.* 20–200°C [composition/wt-%: n-alkanes (C_4–C_{12}), 30; branched-chain alkanes (C_4–C_{12}), 30; naphthenes (C_5 C_{12}), 25; and aromatics (C_6–C_9), 15] is passed through a coiled reactor held at 750–900°C; essential operating conditions include a short residence time (0.1 0.4 s), low overall pressure ($< 3 \times 10^5\ N\ m^{-2}$), low hydrocarbon partial pressure (steam dilution 25–100 wt-%), and rapid quenching of product (to 300–400°C) to minimize secondary reactions. A typical naphtha-based product (cracking temperature, 870°C; single-pass operation) comprises (yields/wt-% also provided): H_2, 1.0; CH_4, 19.2; $CH{\equiv}CH$ (acetylene or ethyne), 0.6; $CH_2{=}CH_2$, 32.2; C_2H_6, 4.7; $CH_3CH{=}CH_2$ (propylene or propene), 14.6; C_3H_8, 0.4; C_4 hydrocarbons [butanes, butenes (butylenes), and butadiene], 7.6; gasoline, 15.0; fuel oil, 4.0. The gasoline fraction, known as pyrolysis gasoline, is an important source of aromatics.

Ethylene is produced most efficiently from the n-alkanes (straight-chain paraffins) present in the naphtha, a situation readily understood when one considers the reaction mechanism involved.

Thermal decomposition of an n-alkane $RCH_2CH_2CH_2R'$ (R,R′ = alkyl groups) proceeds via a radical chain reaction (eqn (1)) initiated by homolytic cleavage of the weakest* C—C bond†:

$$RCH_2\overset{\curvearrowleft}{CH_2}\!-\!\overset{\curvearrowleft}{CH_2}R' \longrightarrow RCH_2\dot{C}H_2 + \dot{C}H_2R' \qquad (1)$$

(Similar unimolecular fission of C—H bonds, e.g.

$$RCH_2CH_2CH_2R' \longrightarrow R\dot{C}HCH_2CH_2R' + H\cdot$$

is generally insignificant.) Propagation reactions then occur in which the primary alkyl radicals generated in the initiation step partake in one or more of the following processes:

(2) *Fragmentation* to yield ethylene and a new alkyl radical [or hydrogen atom if the radical in question is the ethyl radical (R = H)]; since the C—C bond *beta*

$$R\!-\!\overset{\curvearrowleft}{CH_2}\!-\!\overset{\curvearrowright}{\dot{C}H_2} \xrightarrow{\beta\text{-fission}} R\cdot + CH_2{=}CH_2 \qquad (2)$$

* Examples of some relevant bond dissociation energies, D (enthalpies per mole required to break homolytically given bonds in specific chemical species), are: $D(H_3C{-}CH_3)$ 368, $D(H{-}CH_3)$ 435; $D(H_3C{-}C_2H_5)$ 356, $D(H{-}C_2H_5)$ 410; $D(H_3CH_2C{-}CH_2CH_3)$ 343, $D(H_3C{-}CH_2CH_2CH_3)$ 356 kJ mol^{-1}.

† The 'half-arrow' notation ($\curvearrowleft$) shown here is a pictorial aid often employed to indicate the origin and point-of-arrival of a single electron. It is often more convenient to employ the less instructive 'dashed-line' notation to indicate homolytic cleavage of a bond, as in Schemes 1 and 2. Half-arrows must not be confused with normal curved arrows ($\curvearrowright$) associated with the origins and points of arrival of electron pairs, and used later in the discussion of mechanisms involving *heterolytic* bond-cleavages.

to the radical site undergoes homolysis, this type of reaction—common in radical chemistry—is often referred to as β-fission (or β-scission).

(3) *Abstraction* of hydrogen atom from undissociated feedstock; this type of reaction, in which formation of a 2° alkyl radical is preferred (via attack on a

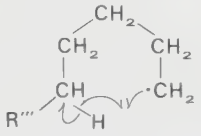
$$RCH_2CH_2CH_2R' \xrightarrow{R''\cdot} \dot{R}CHCH_2CH_2R' + R''H \qquad (3)$$

$$[R''\cdot = RCH_2CH_2\cdot,\ R'CH_2\cdot,\ \text{or}\ R\cdot\ (\text{see eqn (2)})]$$

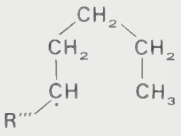
methylene group, $—CH_2—$) to formation of a less stable 1° radical (via attack on a methyl group, $—CH_3$), clearly is one in which radicals ($R\cdot$) formed in eqn (2) will participate. The 2° radicals ($R\dot{C}HCH_2CH_2R'$) thus produced can yield higher homologues of ethylene via β-fission (cf. eqn (2)):

$$R\dot{C}H—CH_2—CH_2R' \xrightarrow{\beta\text{-fission}} RCH{=}CH_2 + \cdot CH_2R'$$

(4) *Rearrangement*, if their structures allow, via intramolecular hydrogen abstraction to yield 2° radicals:



(1°)



(2°)

(4)

This process will be followed by fragmentation of the new radical:

$$R'''\dot{C}H—CH_2—CH_2CH_2CH_3 \xrightarrow{\beta\text{-fission}} R'''CH{=}CH_2 + \cdot CH_2—CH_2—CH_3$$

$$\cdot CH_2—CH_2—CH_3 \xrightarrow{\beta\text{-fission}} CH_2{=}CH_2 + \cdot CH_3 \longrightarrow \text{to eqns (3) or (5)}$$

the consecutive occurrence of several β-fissions being referred to as 'unzipping' of the alkyl chain.

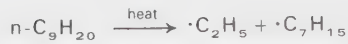
(5) *Coupling* or *disproportionation* of 'small' radicals, leading to termination of the chain reaction, e.g.

$$\left.\begin{aligned} 2\cdot CH_3 &\xrightarrow{\text{coupling}} CH_3—CH_3 \\ \dot{C}H_2—CH_2—H\cdot\cdot CH_3 &\xrightarrow{\text{disproportionation}} CH_2{=}CH_2 + CH_4 \end{aligned}\right\} \qquad (5)$$

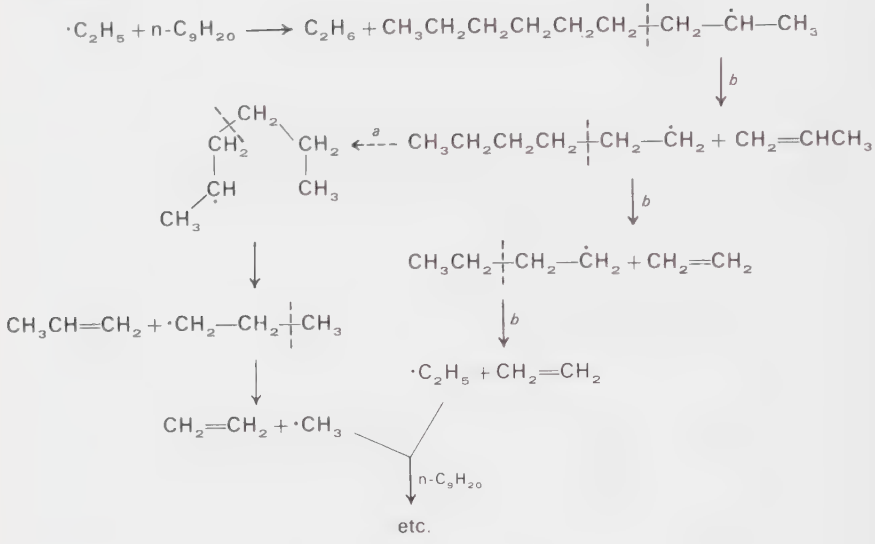
Use of steam as a diluent reduces the hydrocarbon partial pressure, thereby favouring the unimolecular initiation and β-fission reactions at the expense of termination and other bimolecular reactions involving reactive chain carriers (eqn (3)). The complete thermal cracking sequence is illustrated in Scheme 1 for n-nonane.

Obviously the situation becomes much more complex when one considers the steam-cracking of whole naphtha and not just its n-alkane components.

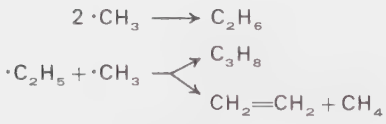
Initiation



Propagation



Termination



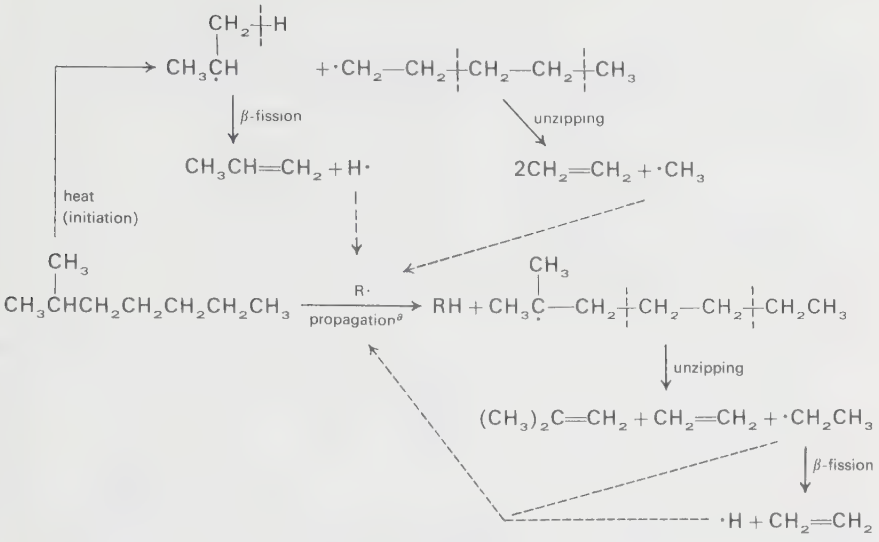
SCHEME 1.

[a] See eqn 4 (p. 303; R‴ = CH_3).
[b] An unzipping sequence.

However, the mechanistic ideas presented above are easily extended to explain, for example, why branched-chain alkanes present in naphtha give lower yields of ethylene than do the n-alkanes (see Scheme 2); why naphthenic naphthas (naphthas containing a high proportion of cycloalkanes) give higher yields of buta-1,3-diene (and lower yields of ethylene) than paraffinic naphthas (see Scheme 3); and how condensation and oligomerization reactions can intervene to give polynuclear aromatics and hence coke. For further details, readers should consult the books by Wiseman and Tedder, Nechvatal/Jubb (see p. 327). Ethane cracking can be rationalized by the relatively simple mechanism shown in Scheme 4.

Catalytic Cracking

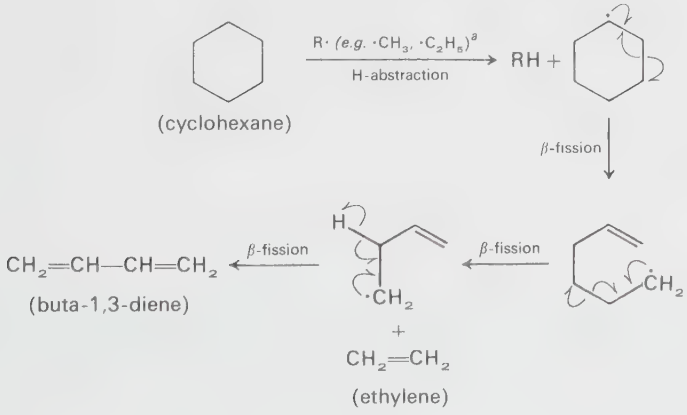
This process, introduced in 1936, is employed to convert heavy oils ('vacuum distillate', boiling range 350–550 °C, and to some extent 'gas oils', boiling range



SCHEME 2.

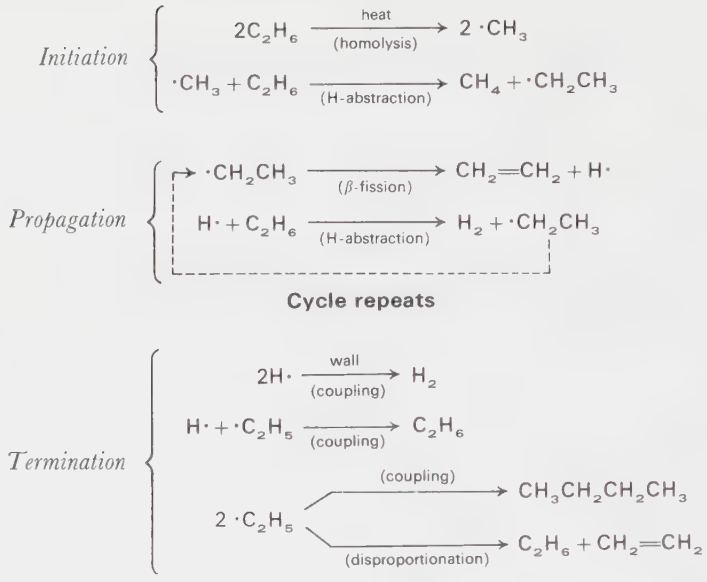
[a] Naturally, radicals from any source can be involved here.

250–350°C) into high-octane-number gasoline; some gaseous products, notably propene and butenes, are produced but, in contrast to thermal cracking, ethylene is a minor component. Catalytic cracking is carried out with steam-carried feed at about 450 to 550°C and approximately atmospheric pressure in fixed- or fluidized-bed reactors containing synthetic silica-alumina (SiO_2–Al_2O_3) or, more importantly nowadays, synthetic zeolites (or molecular sieves—crystalline aluminosilicates). Coke deposits on the catalyst, so provision has to be made to remove it by oxidation with air. The catalysts



SCHEME 3.

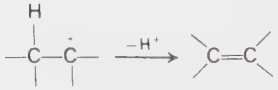
[a] Radicals from any source (see Schemes 1 and 2) can be involved here.



Scheme 4.

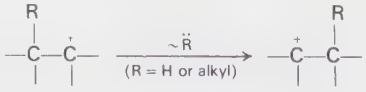
possess acidic characters [Brønsted (proton donors) and Lewis (electron-pair acceptors)] and their function is to initiate and maintain a series of reactions involving ionic intermediates of the carbocation type.

Knowledge of the detailed mechanisms of catalytic cracking of even individual components of heavy oils is still incomplete, so the discussion here is restricted to providing *model* pathways to exemplify the types of reaction thought to contribute to molecular weight reduction, aromatization, and cyclization; this is done in Schemes 5, 6, and 7, where plausible pathways associated with conversions of an n-alkane, an alkylcycloalkane, and an alkylaromatic, respectively, are *outlined*. These are based on well-established types of reactions undergone by electron-seeking carbenium ions, namely, *β-elimination of a proton* (eqn (6), loss of a proton from a carbon atom adjacent to

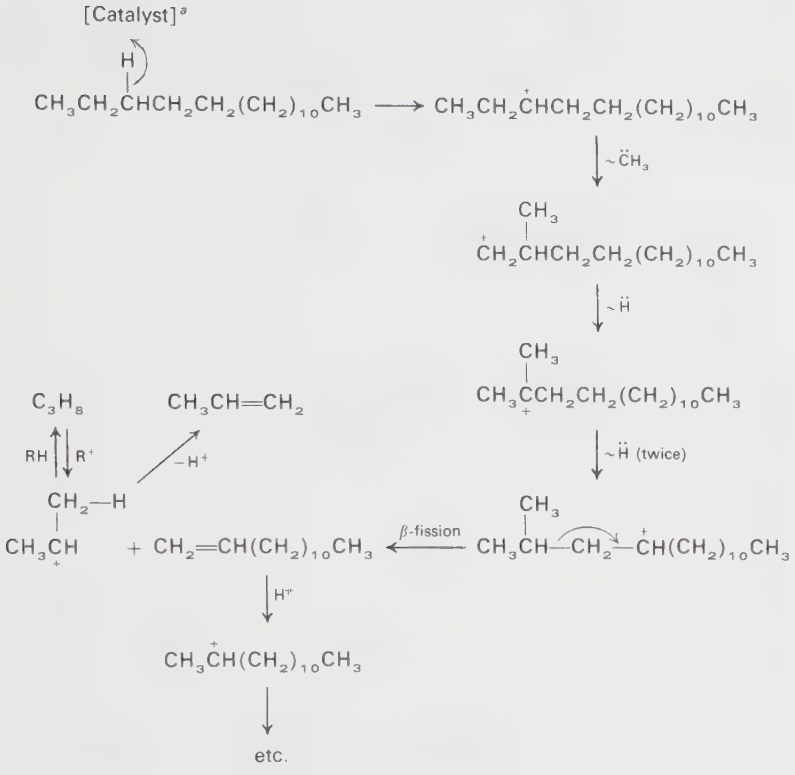


(6)

the cationic centre), *internal rearrangement* via 1,2-hydrogen ($\sim\ddot{H}$) or 1,2-alkyl (e.g. $\sim\ddot{C}H_3$) shifts (eqn (7); migration of substituents, complete with bonding electrons, to the cationic centre from a β-position), *abstraction* of hydride ion

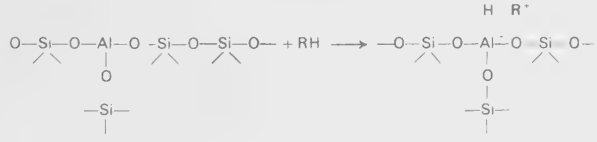


(7)



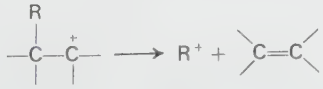
SCHEME 5.

[a] Often visualized simply as removal of hydride ion from the alkane by Lewis acid sites of the catalyst, i.e.



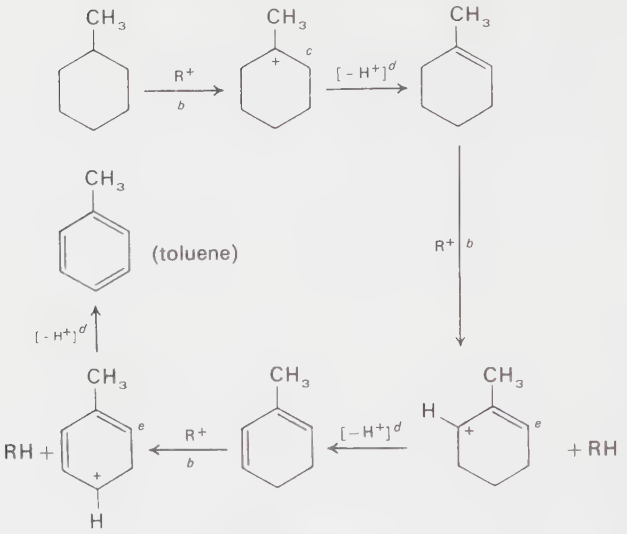
from another molecule (RH) (eqn (8)), and skeletal fragmentation via β-fission (eqn (9)).

(8)



(9)

Addition of a carbenium ion (an electrophile) to neither an olefin (eqn (10); the reverse of eqn (9)) nor an aromatic (eqn (11)) features in Schemes 5–7,



SCHEME 6.[a]

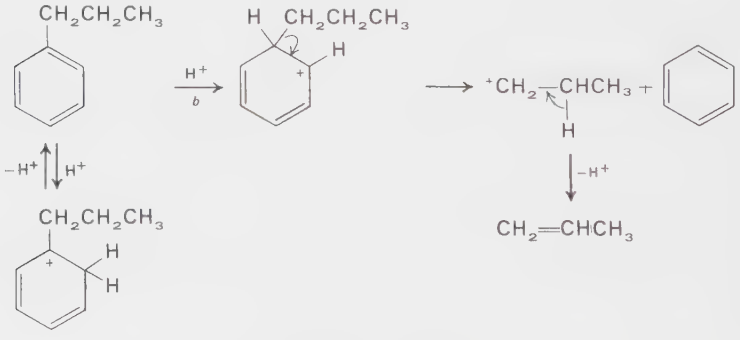
[a] In principle, all the steps are reversible.

[b] Or Cat → [CatH]$^-$ (see footnote *a*, Scheme 5); R^+ = an alkyl cation generated, for example, from an alkane or an olefin.

[c] This 3° carbocation will be formed in preference to a 2° (H^- abstraction from the CH_3) one.

[d] Transferred to a proton acceptor, e.g. an olefin (see Scheme 5), [CatH]$^-$, or an aromatic (see Scheme 7).

[e] These carbocations are of lower energy than the 3° carbocation formed in the first step owing to a resonance effect (see footnote, p. 309); thus, hydride ion is more readily removed from their immediate precursors than from the feedstock.



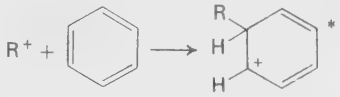
SCHEME 7.[a]

[a] The order of ease of removal of an alkyl group (R) in PhR is consistent with the order of stability of the alkyl cations produced, e.g. $(CH_3)_3C^+ > C_2H_5\overset{+}{C}HCH_3 > CH_3CH_2\overset{+}{C}H_2$(3° > 2° > 1°).

[b] The proton can be derived directly from a Brønsted acid site of a zeolite or SiO_2-Al_2O_3 catalyst. When the attacking electrophile (proton) becomes attached to the ring carbon carrying the substituent, *ipso* (see p. 288 for the labelling of ring positions [*ipso* = itself (Latin)] attack is said to have occurred. As illustrated above for *ortho* attack, attachment of the proton at any other ring position cannot lead to dealkylation. Note that cations (cyclohexadienyl cations) generated by protonation of benzene nuclei are resonance-stabilized (cf. footnote *e*, Scheme 6).

although such reactions doubtless occur when crude oil fractions are cracked catalytically. The same must be true for skeletal fragmentation (cf. p. 304) of bicyclic naphthenes and cycloalkylaromatics.

(10)



(11)

Since only small amounts of ethylene are formed via catalytic cracking, β-fission of primary carbenium ions ($C_nH_{2n+1}CH_2CH_2^+ \rightarrow {}^+C_nH_{2n+1} + CH_2{=}CH_2$) is judged not to compete effectively against other possible fates, notably isomerization via 1,2-H shifts (eqn (7); R = H) to more stable secondary cations and hydride-abstractions (eqn (8)). Beta C—C fission (eqn (9)) occurs most readily when structural features allow a tertiary carbenium ion to be ejected.

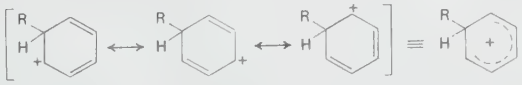
Hydrocracking

This refinery process is simply a combination of catalytic cracking and catalytic hydrogenation at high pressures using dual-function catalysts, e.g. nickel on silica-alumina. Lower operating temperatures can be employed because initiation of reaction via dehydrogenation of alkanes to alkenes, followed by protonation of the latter, is possible (eqn (10), $R^+ = H^+$). Since hydrogen is available, alkenes produced via catalytic cracking processes (Scheme 5) are converted into alkanes.

Catalytic Reforming

This and catalytic cracking are the two most important conversion processes operated by modern oil refineries. Its main function is to raise the octane number (ON) of straight-run naphtha boiling in the range 70 to 90 °C (aromatization—see below—requires $\geq C_6$ hydrocarbon feedstock) from a value in the *ca.* 20–50 region to one in keeping with material (85–95 range) required for the provision of high-octane motor gasoline. Such ON 'jumps' are achievable largely because non-aromatics are converted into aromatic components, and from this stems the importance of catalytic reforming as a source of primary petrochemicals of the arene class. Consideration of ON values for pure hydrocarbons reveals that conversion of straight-run naphtha

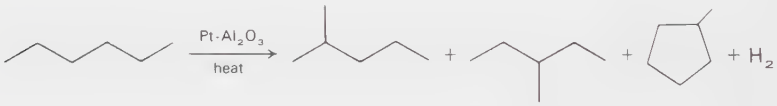
* This carbocation is stabilized by a resonance effect, delocalization of the unit positive charge being possible owing to the conjugated structure:



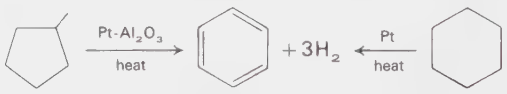
Only one canonical form is presented here and elsewhere in the main text for such species.

into high-octane gasoline could be achieved in four ways: increase the concentration of (i) aromatics, (ii) branched alkanes, or (iii) alkenes; and (iv) decrease the average molecular weight. In practice, the presence of alkenes leads to engine fouling, and decrease in molecular weight confers too high a volatility on the gasoline; this leaves aromatization and isomerization, and it is these reformation reactions which are maximized (particularly the former) in current processes. These utilize platinum–alumina catalysts known as *dual-function catalysts* because they possess both hydrogenation–dehydrogenation and acidic (carbocation-forming) properties. Typical operating conditions are temperatures in the range 500 to 525 °C, pressures of *ca.* 25 atm, and a naphtha:hydrogen ratio of 1:6. Feedstock is desulphurized (to <3 ppm S) prior to reforming to prevent deactivation of the platinum component of the catalyst which, typically, comprises 0.3 wt-% Pt on acidic Al_2O_3 promoted with *ca.* 1 wt-% of chlorine. Use of hydrogen, while not favouring dehydrogenation of cyclohexanes to aromatics, suppresses formation of carbonaceous material ('coke') which settles on, and deactivates, the catalyst.

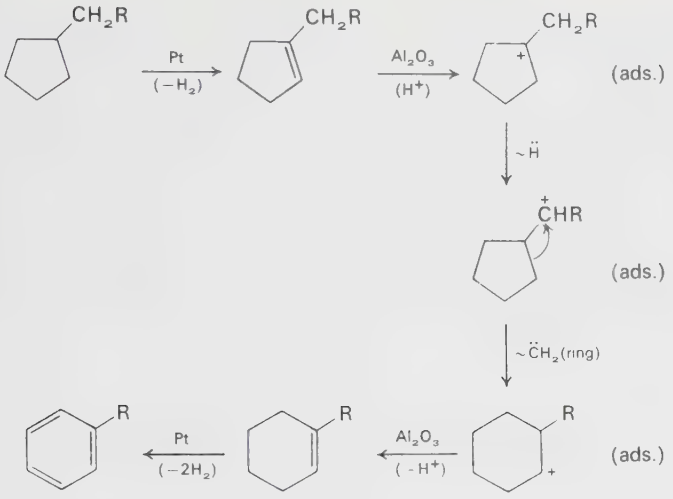
The main reactions which occur during catalytic reforming are *isomerization*, *dehydrocyclization*, *dehydrogenation*, and *hydrocracking*. Alkanes undergo skeletal isomerization and dehydrocyclization to naphthenes, for example



and are hydrocracked to lower homologues. Alkylcyclopentanes and alkylcyclohexanes undergo skeletal and positional isomerization, and C_6 compounds are rapidly dehydrogenated to arenes, for example

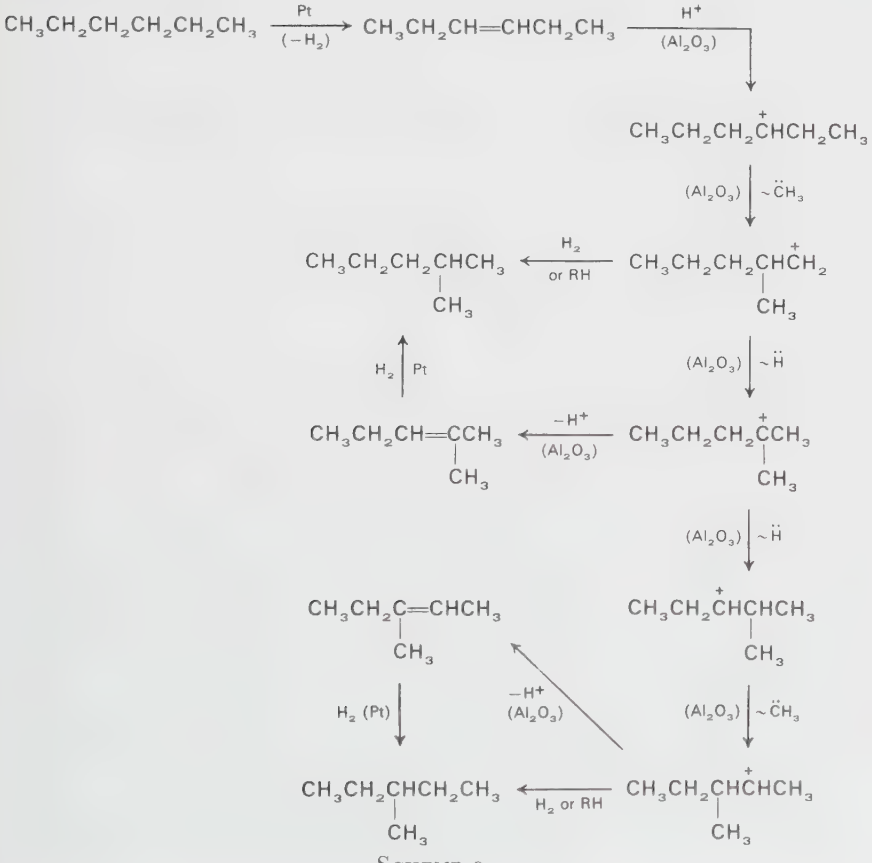


Minor reactions include hydrogenation of arenes to cycloalkanes and dealkylation of alkylcycloalkanes. Reforming reactions are believed to proceed sequentially over the metallic and acidic sites of the dual-function catalyst. Experiments with individual C_6 and C_7 alkanes and cycloalkanes in the presence of platinum-on-silica, platinum-on-inert alumina, or platinum alone have revealed that dehydrocyclization of alkanes to alkylcyclopentanes and dehydrogenation of cyclic C_6 compounds to arenes [$C_6H_{11}R \rightleftharpoons C_6H_5R$ ($R = H$ or CH_3) $+ 3H_2$] are platinum-catalysed processes. Mediation by the acidic components of dual-function catalysts is required for direct (i.e. no participation from cyclic entities) isomerization of acyclic compounds (alkane $\rightleftharpoons$ branched alkanes) and skeletal isomerization of cyclic compounds (alkylcyclopentanes $\rightleftharpoons$ alkylcyclohexanes); these reactions are easily visualized in terms of carbocationic transformations initiated via protonation of olefins arising from dehydrogenations encouraged by the platinum of the dual-function catalyst (see Schemes 8 and 9). Much more work remains to be done before a detailed comprehensive mechanism of catalytic reforming can be advanced.



SCHEME 8.[a]

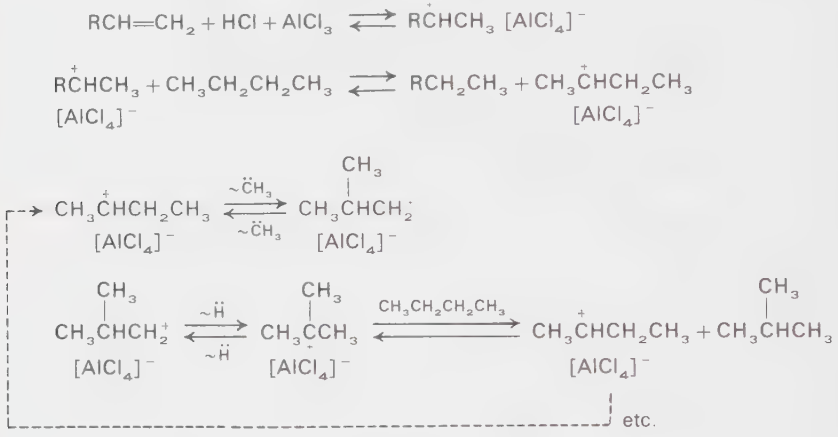
[a] (ads. = Adsorbed on the catalyst.



SCHEME 9.

Isomerization

In the oil industry, catalytic isomerization refers to carbocation-mediated reactions leading to conversion of C_4–C_7 normal alkanes to their branched counterparts. A Friedel–Crafts catalyst system is employed to effect skeletal rearrangement of n-butane to isobutane, whereas a modified catalytic reforming procedure best suits the conversion of C_5–C_7 range straight-run naphtha (boiling range 30–70°C) to high-octane-number material. The outcome of each type of procedure is easily rationalized in terms of carbenium-ion intermediates, initiation of reaction in the $n\text{-}C_4H_{10} \rightarrow i\text{-}C_4H_{10}$ case requiring the presence of traces (<0.1 per cent) of olefinic material ('promoter') in the feedstock (see Scheme 10).


RCH=CH2 + HCl + AlCl3 ⇌ RCHCH3 [AlCl4]−
RCHCH3 + CH3CH2CH2CH3 ⇌ RCH2CH3 + CH3CHCH2CH3
[AlCl4]− [AlCl4]−
CH3CHCH2CH3 ⇌ CH3CHCH2
[AlCl4]− [AlCl4]−
CH3CHCH2 ⇌ CH3CCH3 → CH3CHCH2CH3 + CH3CHCH3
[AlCl4]− [AlCl4]− [AlCl4]−
etc.

Scheme 10.

Alkylation and Polymerization

From an oil refinery viewpoint, alkylation—a general term in organic chemistry meaning the introduction of one or more alkyl groups into an organic molecule—refers specifically to the acid-catalysed reaction of an alkene with an alkane. Industrial operations are based on the conversion of isobutane and C_3–C_5 alkenes (i.e. cracking operation by-products) into high-octane gasoline components, with 98 per cent sulphuric acid (at 4–15°C and a pressure slightly higher than atmospheric) or hydrogen fluoride (at 25–45°C and 100–150 psi) as the catalyst. The products ('alkylates') are complex, e.g. under one set of conditions isobutane reacts with propene in the presence of hydrogen fluoride at 38°C to give an alkylate comprising the following alkanes: $CH_3CH_2CH_3$ (25 per cent), $(CH_3)_2CHCH(CH_3)CH_2CH_3$ (37.5 per cent), $(CH_3)_2CHCH_2CH(CH_3)_2$ (18.5 per cent), $(CH_3)_3CCH_2CH(CH_3)_2$ ('isooctane', 11 per cent), $(CH_3)_2CHCH(CH_3)CH(CH_3)_2$ (3.5 per cent), $(CH_3)_2CHC(CH_3)_2CH_2CH_3$ (2 per cent), and $(CH_3)_3CCH(CH_3)CH_2CH_3$ (0.5 per cent). The situation is that extensive isomerization always accompanies alkylation, and so-called secondary reactions occur which lead, for example, to the formation of both C_7 and C_8 alkanes from a C_4 alkane and a

C_3 alkene. Mechanistic scenarios of the carbenium ion type provide explanations, as exemplified in Scheme 11 (see page 314) (the products, also shown above, are 'boxed').

Note that during alkylation, polymerization of the alkene can occur (e.g. see Scheme 12, see page 316); this is undesirable because it increases consumption of the alkene, which is normally more valuable than isobutane. Thus, polymerization is minimized by using an excess of the alkane to encourage hydride transfer at the expense of propagation. Isobutane is a good transfer agent because a tertiary carbenium ion $[(CH_3)_3C^+]$ can be produced from it; n-alkanes like butane and pentane, which can yield only secondary or primary carbenium ions (in that order of preference from a relative stability viewpoint) do not partake in alkylation reactions with alkenes under the refinery conditions outlined above.

CRUDE OIL CLASSIFICATION AND HYDROCARBON TYPE ANALYSIS

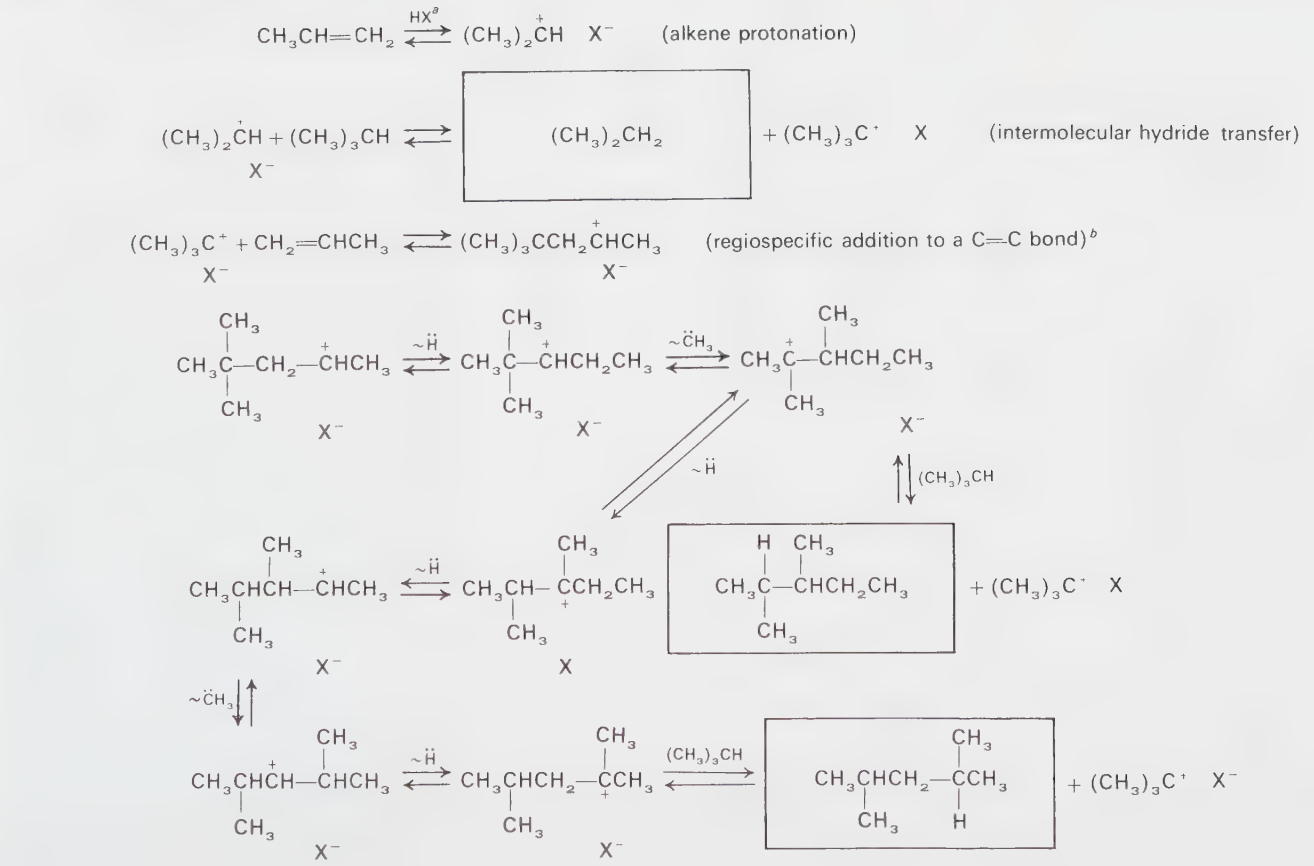
A method of classifying crude oils is necessary to provide a guide to the quality, and hence value, of the oil. In the very early days the kerosine fraction used for lighting purposes was the most valuable product. With the introduction of the internal combustion engine, gasoline became the most valuable fraction in crude oil. The specific gravity of a crude oil provided a rough measure of the amount of the lighter fractions present; the lower the specific gravity (or the higher the API gravity, which is an inverse scale) the greater was the yield of light fractions by simple distillation, and hence the higher the price of the crude.

With the introduction of more sophisticated procedures, and particularly the introduction of cracking processes, the rough guide provided by specific gravity was insufficient to classify oils. Moreover, further information on the nature of an oil and some indication of the chemical composition, both of the crude and of the various fractions which could be produced from it, became necessary. The first attempt to provide such information was the use of the concept of the 'base' of a crude oil.

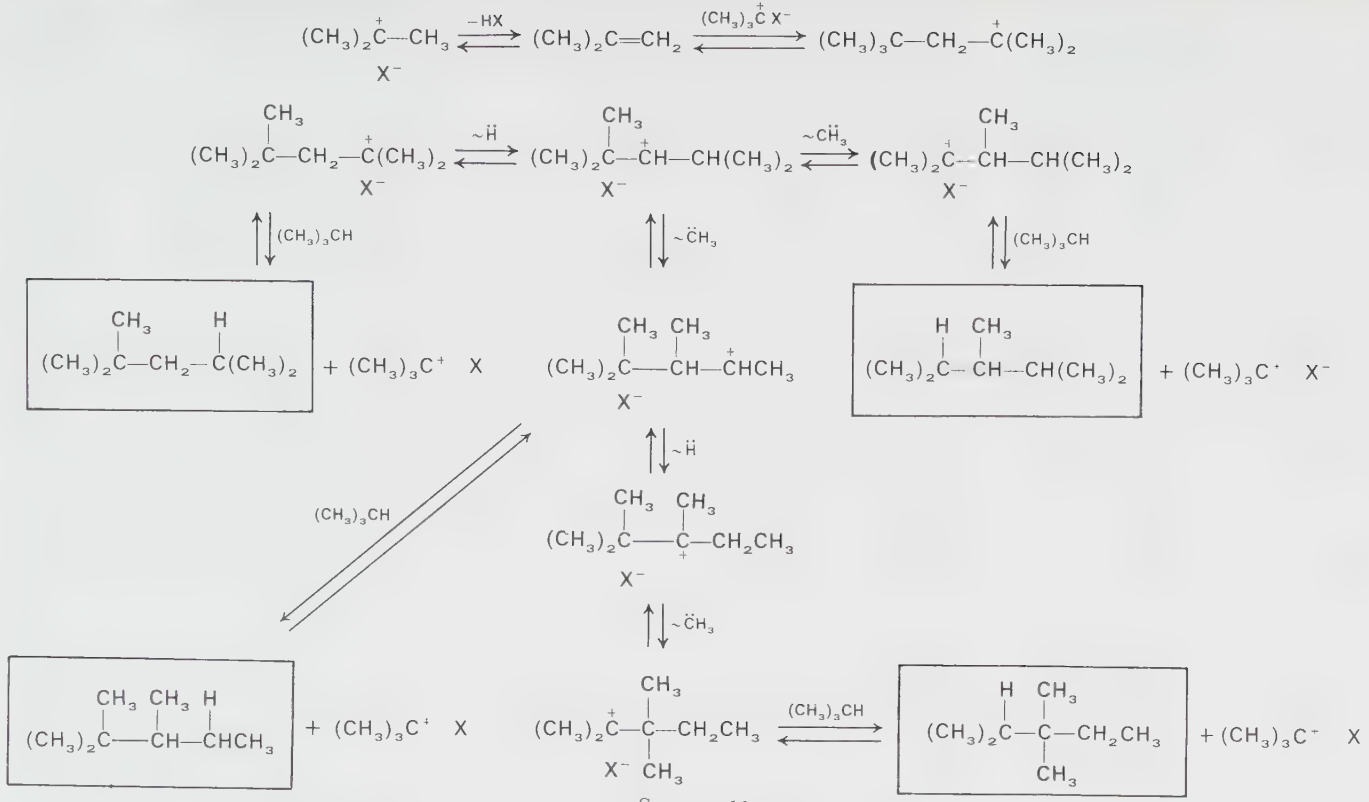
It had been noted that solid wax separated when the atmospheric distillation residues of Pennsylvanian crudes were cooled. Similar residues from Texan or Californian crudes did not deposit wax on cooling, and were found to contain asphaltic material. These observations led to a differentiation between 'wax-bearing' and 'wax-free' crude oils, or between 'paraffinic base' and 'asphaltic base' crude oils. Intermediate between these two types of crude were many oils which on distillation yielded residues containing both paraffin waxes and asphaltic material, these were termed 'intermediate base' crudes.

Taking into account the three types of crude and their specific gravity (light or heavy), a main scheme of general classification was established which, in general terms, still stands. This scheme was later enlarged to accommodate a fourth group of crudes of 'hybrid base', whose residue on atmospheric distillation contained asphaltic material with small amounts of paraffin wax, and which were described as 'naphthenic' crudes. Used in this context the term 'naphthenic' is quite misleading, as it is not related to the hydrocarbon type of the same name discussed previously (p. 285).

'Normal' reaction sequence



'Abnormal' reaction sequence (secondary reactions)



SCHEME 11.

[a] $HX = H_2SO_4$ ($X^- = HSO_4^-$) or $(HF)_n[X^- = (H_{n-1}F_n)^-]$.

[b] So-called Markovnikov addition, in which the direction of addition of an electrophile to an unsymmetrically-substituted alkene linkage (C=C) proceeds to give predominantly, or even exclusively, the more stable of the two possible carbenium ions [$(CH_3)_2\overset{+}{C}H$ (2°) versus $CH_3CH_2\overset{+}{C}H_2$ (1°) in this case; $(CH_3)_3C^+$ (3°) versus $(CH_3)_2CH\overset{+}{C}H_2$ (1°) in the case of isobutene].

$$(CH_3)_2C{=}CH_2 \xrightarrow{HX} (CH_3)_3C^+X^- \xrightarrow{(CH_3)_2C=CH_2}$$

$$(CH_3)_3C{-}CH_2\overset{+}{C}(CH_3)_2X^- \xrightarrow{(CH_3)_2C=CH_2} (CH_3)_3C{-}CH_2C(CH_3)_2{-}CH_2\overset{+}{C}(CH_3)_2X^- \longrightarrow \text{etc.}$$

Scheme 12.

Following this qualitative classification, several attempts were made to devise classifications based on chemical analysis or on the physical properties as an indication of the chemical composition of a given narrow distillation fraction, but without success. The main obstacle was the impossibility of characterizing a whole crude by the characteristics of a single fraction, since the chemical character of the successive fractions obtained by distillation of the oil can and does change as the boiling range of the fraction increases.

In 1937 Lane and Garton of the US Bureau of Mines put forward a general scheme for the classification of crudes based on the specific gravity of two fractions (*key fractions*) produced by a standardized method of fractionation of the crude. Although this classification is not completely satisfactory, it is now universally employed. The main advantage lies in the wide coverage, since practically all known crude oils have been analysed and classified by this method and the information is kept up to date by the periodic publication of new analyses by the US Bureau of Mines.

The method involves fractionation of the crude, starting by a distillation at atmospheric pressure, during which the fraction boiling between 250 and 275°C is collected (key fraction No. 1), and continuing with a distillation at 40 mmHg during which the fraction boiling between 275 and 300°C is collected (key fraction No. 2). The specific gravity of both fractions is determined, and from the specific gravity (or API gravity) of the fractions, the crude is assigned to one of the nine classes shown in Table II.

Characterization of Petroleum Fractions

In the last forty years the whole field of chemical analysis has developed at an extremely rapid pace. Detection and estimation of single components in very complex natural products, like petroleum fractions, once considered impossible, are nowadays carried out as a matter of routine in plant laboratories with very accurate results. Two main factors acccount for this change: the development of new analytical/separation techniques, particularly chromatographic methods—notably gas–liquid chromatography and high-pressure liquid chromatography; and developments in instrumentation which have made available a whole range of fast, reliable and relatively cheap spectrometers (i.r., u.v., n.m.r., mass) and coupled gas chromatograph—mass spectrometers.

But, in spite of all the advances, knowledge of the constitution of some petroleum fractions is still very fragmentary, particularly in the region of residual oils and asphaltic materials. Furthermore, in the case of fractions for which the total analysis is practicable, the very wealth of information possible is

TABLE II

Classification of Crude Oils According to the US Bureau of Mines

Class	Key fraction No. 1		Key fraction No. 2	
	Sp gr 60/60°F	° API	Sp gr 60/60°F	° API
Paraffinic	<0.825	≥40	<0.876	≥30
Paraffinic–Intermediate	<0.825	≥40	0.876–0.934	20–30
Intermediate–Paraffinic	0.825–0.860	33–40	<0.876	≥30
Intermediate	0.825–0.860	33–40	0.876–0.934	20–30
Intermediate–Naphthenic	0.825–0.860	33–40	>0.934	≤20
Naphthenic–Intermediate	>0.860	≤33	0.876–0.934	20–30
Naphthenic	>0.860	≤33	>0.934	≤20
Paraffinic–Naphthenic	<0.825	≥40	>0.934	≤20
Naphthenic–Paraffinic	>0.860	≤33	<0.876	≥30

difficult to interpret for the purposes of plant design or operation. In such cases use is made of simpler, even if less accurate, methods of characterization.

One group of such methods uses functions based on a set of physical constants, to describe, by means of factors or indices, the predominant chemical character of a petroleum fraction.

The second group, comprising the methods of structural group analysis, describes the character of the fraction in terms of elements constituting an imaginary average molecule having the chemical and physical properties of the sum of the individual components of the fraction, according to their concentration.

Characterization Functions

Characterization factor

This factor, K, devised by members of the Universal Oil Products Co., is based on data for pure hydrocarbons, and correlates boiling point with specific gravity, according to the following expression:

$$K = T_B^{1/3}/d$$

where T_B is the boiling point in degrees Rankine (degrees Fahrenheit plus 460) or, in the case of a fraction, its average boiling point, and d is the specific gravity at 60/60°F. The average boiling point of a fraction is obtained from the IP/ASTM distillation curve by averaging the temperatures at which the 10, 30, 50, 70, and 90 per cent volumes distil and applying a small correction for the slope of the distillation curve. This characterization factor is additive on a weight basis for mixtures or blends.

Values of K between 12.5 and 13.0 are found for paraffinic hydrocarbons, between 11.0 and 12.0 for naphthenic hydrocarbons, and between 9.0 and 12.0 for aromatics. Thus, high values of K for a petroleum fraction indicate that its components are predominantly paraffinic in nature, while low values of K indicate that aromatics predominate.

This factor is of widespread use, mainly on account of the complementary correlations developed between K and other properties such as hydrogen

content, viscosity-gravity constant, specific heat, etc., as well as between K of feedstocks and yields of products by processes operating at specified conditions, such as thermal cracking, furnace black production, etc.

Correlation Index

This index (CI) developed by the US Bureau of Mines, is based on the plot of specific gravity at 60/60 F versus the reciprocal of the boiling point in Kelvin (degrees Celsius plus 273) for pure hydrocarbons on which the line described by the constants of the individual members of the normal paraffin series is given a value of CI = 0 and a parallel line passing through the point for the values of benzene is given as CI = 100. From this graph the following empirical equation is derived:

$$\mathrm{CI} = 473.7d - 456.8 + 48\,640/K$$

in which, K in the case of a petroleum fraction, is its average boiling point, determined by the standard Bureau of Mines distillation method.

Values for the index between 0 and 15 indicate a predominance of paraffinic hydrocarbons in the fraction; from 15 to 50 a predominance either of naphthenes or of mixtures of paraffins, naphthenes and aromatics; above 50 indicates predominantly aromatic character.

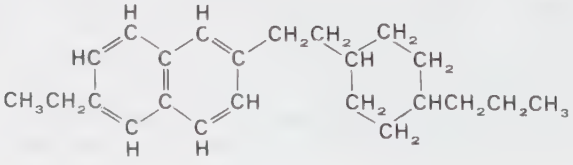
The main usefulness of the index lies in the complementary information it provides on the fractions produced in the Bureau of Mines crude oil assay already mentioned, particularly in the atmospheric distillation range.

Other physical characteristics are used to establish correlations of a more limited application to specific ranges of products, such as the Viscosity-Gravity constant, for the lubricating oils range, the Diesel Index of the fuels for compression-ignition engines, etc.

Structural Group Analysis Methods

It has already been stated that the main constituents of petroleum are hydrocarbon molecules containing either isolated or integrated paraffinic chains, aromatic rings and naphthenic rings. The constitution and the characteristics of a given fraction (average molecular weight, carbon and hydrogen content, density, refractive index, etc.) would be the statistical average of the characteristics of the individual components of the fraction. Thus, the fraction could be imagined as consisting of molecules of a single hypothetical component having the constitution and the characteristics of this statistical average.

If the following structural formula represents the constitution of either a single component or the hypothetical statistical average molecule of a complex



mixture, its analysis could be reported in terms of the carbon skeleton as follows.

Of the 23 carbon atoms it contains, 10 are in aromatic rings, 7 in paraffinic chains and 6 in naphthenic rings. Furthermore, the molecule contains three carbon rings, two of which are aromatic and one is naphthenic. This information, presented in tabular form, reads:

% carbon in paraffinic chains	$\%CP = 30.4$
% carbon in aromatic rings	$\%C_A = 43.5$
% carbon in naphthenic rings	$\%C_N = 26.1$
% carbon in rings	$\%C_R = 69.6$
Total number of rings	$R_T = 3$
Aromatic rings	$R_A = 2$
Naphthenic rings	$R_N = 1$

From this idea, Waterman and co-workers developed the Direct Method of analysis. As the name indicates, the structural elements of the average molecule are determined directly. The method consists of the determination of the average molecular weight of the sample by the ebullioscopic technique, and the percentage of carbon and hydrogen by elemental analysis, both before and after complete hydrogenation.

From the increase in molecular weight and in hydrogen content, taking into account that each aromatic 'double bond' becomes saturated by the addition of two hydrogen atoms, the $\%C_A$ is calculated. From the hydrogen content after hydrogenation and the carbon content, the total number of rings, R_T, can be obtained.

The assumption that the rings are formed by six carbon atoms and that if more than two rings are present they are *ortho*-condensed, allows the calculation of $\%C_R$ from the total number of rings, R_T, and also the number of aromatic rings, R_A. The rest of the structural elements, $\%C_P$, $\%C_N$, and R_N, are obtained by difference from the calculated values.

The Direct Method is elegant and unambiguous—taking into account the fundamental assumptions—but it is very lengthy and requires highly skilled analysts. A much simplified development is the *n–d M* method of van Nes and van Westen, based on the correlation of results obtained from the application of the Direct Method to a large number of fractions of crudes of different origin and constitution, and their refractive indices, densities, and molecular weights. The authors were able to obtain linear relations of the type

$$\%C = a/M + b\,\Delta d + c\,\Delta n$$

where $\%C$ is the percentage of carbon in paraffinic, naphthenic or aromatic structures, as determined by the Direct Method; a, b, and c are constants, different for each type of structure; Δd and Δn the differences in density and refractive index between the values measured in the sample and those for the theoretical hydrocarbon of the corresponding structure and infinite molecular weight.

Further simplifications of methods of structural analysis have appeared in the literature, for instance replacing the determination of molecular weight of

the sample by the logarithm of the viscosity (the *v–n–d* method) or methods correlating the absorptivity of the sample at specific wavelengths of the infrared spectrum and the results of the *n–d–M* analysis on the same sample.

An interesting outcome of these methods of structural analysis is the presentation of the results as a graph—the so-called carbon spectrum—for a series of related samples. By this technique, changes occurring in the chemical composition of the fraction in the course of a process (distillation, extraction, crystallization, etc.) are easily detected and determined.

PHYSICAL PROPERTIES OF PETROLEUM FRACTIONS

In order to identify a material, and to predict the behaviour of the material in particular circumstances, it is necessary to measure certain properties (usually physical) and to compare the measured values with published tabulated information. In the case of pure substances it is normally a comparatively simple task to calculate the behaviour of the material. However, in the case of mixtures, particularly complex multi-component mixtures, the behaviour of the individual pure compounds does not normally correlate simply with the behaviour of the complete mixture. Thus, when dealing with the complex mixtures of hydrocarbons normally found in petroleum fractions, the average properties of the mixture are often of greater importance than a knowledge of exact chemical composition and of the physical properties of the individual compounds. The object of the present section is to present a brief resumé of the importance of the more common physical properties of hydrocarbon mixtures, together with an indication of how a knowledge of these properties permits predictions to be made about the behaviour of the mixture as a whole.

Density (*d*)

This may be defined as the mass per unit volume and may be quoted in a variety of units. The SI unit of kg/m^3 is related to the more commonly used petroleum industry units as follows:

$$1\ lb/ft^3 = 16.019\ kg/m^3$$
$$1\ lb/UK\ gal = 99.776\ kg/m^3$$
$$1\ lb/US\ gal = 119.83\ kg/m^3$$

The unit as described has an absolute value, but the volume must be determined very accurately. This is normally done by weighing a purpose-designed container (pycnometer) first empty and then filled with a standard fluid, at a fixed temperature. Since the calculation of the volume thus depends on the mass of the same volume of standard fluid and the appropriate density-temperature relationships, it is quite normal to dispense with the absolute density measurement and quote the result in terms of specific gravity. For liquids the most usual units are sp gr 60/60 °F, which is the ratio of the weight of a given volume of liquid to the weight of the same volume of water, both weights being determined at 60°F. Other temperatures are used and 4°C is often used for the water measurement since it is at 4°C that water has its maximum density. Specific gravity, being a ratio, is independent of any system of units, but the temperature used must be given.

Other ways of expressing liquid densities are met in particular industries and in the oil industry reference is often found to API gravities. This is derived from the specific gravity by use of the relationship

$$\text{Degrees API} = \left[\frac{141.5}{\text{Sp gr } 60/60\,^{\circ}\text{F}} - 131.5 \right].$$

There is thus no simple relationship between absolute densities and API gravities, and it is usual to consult tabulated information for such conversions.

Density is temperature-dependent; in most cases a fluid becomes less dense as the temperature rises. Exceptions to this rule are found, presumably when a change in molecular configuration occurs in the fluid. A typical example of this phenomenon is water which shows a maximum density at 4 °C and not, as with most liquids, at its freezing point. There is also a small effect of pressure on liquid densities, although except at high pressure this is not normally significant for hydrocarbon systems. Comprehensive tables showing the variation of density (or of specific gravity) with temperature and pressure are published by the Institute of Petroleum and other bodies.

Vapour densities are defined in the same way as liquid densities, but are very much smaller, and because of this they are often expressed as gravities relative to air at a particular temperature. Unlike liquid densities, vapour densities are very dependent on pressure and it is very important that the pressure involved is accurately reported.

Vapour densities are usually more conventionally expressed in terms of specific volumes, that is as volume per unit mass (m^3/kg or ft^3/lb), and the relationship between specific volume, temperature, and pressure will be discussed separately. However, in the oil industry, vapour density information is sometimes reported in terms of ft^3/gal liquid. Although such combinations of units are of value in certain applications, great care must be taken to ensure that the pressure and temperature of the vapour are known, together with the temperature at which the liquid volume was measured. It is probably better to avoid the use of such units wherever possible.

The main use of density is to permit the mass of a given volume of liquid or gas to be determined for use in subsequent calculations. Knowledge of density is also a guide to chemical composition. Although it is only rarely that density on its own can be used to determine composition, it is often used in combination with other properties to characterize a mixture. In general, paraffinic hydrocarbons have comparatively low densities, naphthenic, and olefinic hydrocarbons intermediate densities, and aromatic hydrocarbons comparatively high densities.

Refractive Index (n)

This is defined as the ratio of the velocity of light in vacuum to the velocity of light of the same wavelength in the substance. It can be measured comparatively easily in a number of instruments most of which utilize the fact that the refractive index is numerically equal to the ratio of the sine of the angle of incidence to the sine of the angle of refraction when light passes obliquely from vacuum into the substance. The value of refractive index varies with the

wavelength of the light used, and also with temperature, and both must be quoted. The '*D* line' of the sodium spectrum (wavelengths of 5890 and 5896 Å) is usually used for refractive index measurements with hydrocarbons.

Refractive index alone can be used to give information on the composition of hydrocarbon mixtures; as with density, low values are associated with paraffins and higher values with aromatics. The combination of refractive index and density is a more powerful tool, and several authorities have proposed the use of such combinations as 'refractivity intercept':

$$\left(n - \frac{d}{2}\right)$$

and 'specific refraction'

$$\left(\frac{(n^2 - 1)}{(n^2 + 2)} \cdot \frac{1}{d}\right)$$

as indicative of the chemical composition of hydrocarbon mixtures. The use of refractive index in the more sophisticated methods of ring analysis has been described in the previous section (p. 319).

Viscosity

The viscosity of a fluid is a measure of the difficulty with which it can be made to flow; it may be thought of as a type of internal friction which prevents a fluid moving as freely as it otherwise would. Dynamic viscosity (μ) may be defined as the force per unit area which is required to maintain a unit velocity gradient in the fluid. If the ratio of the force to the velocity gradient remains constant with increasing velocity (rate of shear) the liquid is said to be Newtonian, and many of the liquids encountered in the petroleum industry do behave in this manner. However, in many other fluids the ratio of the force to the velocity gradient depends strongly on the rate of shear. These fluids are designated as non-Newtonian and may be variously described as dilatant, pseudoplastic, thixotropic, rheopectic, etc., depending on the type of relationship actually encountered. In the present discussion only Newtonian fluids will be considered. The unit of dynamic viscosity is force × time/(length)^2 and hence in SI units is given in N s/m^2. The appropriate conversions for units more common in the petroleum industry are

$$\begin{aligned} 1 \text{ poise (dyne sec/cm}^2) &= 0.1 \text{ N s/m}^2 \\ 1 \text{ lb/ft hr} &= 0.413\,38 \text{ mN s/m}^2 \\ 1 \text{ lb/ft sec} &= 1.4882 \text{ N s/m}^2 \end{aligned}$$

Since viscosity is normally determined by the time of flow of a liquid under its own weight in a capillary of known dimensions, viscosities are also reported in terms of kinematic viscosity (ν) which is defined as the dynamic viscosity divided by the density (μ/d). Thus the unit of kinematic viscosity is force × time × length/mass and in SI units is given as m^2/s. The appropriate conversions are

$$\begin{aligned} 1 \text{ stokes (dyne sec cm/g)} &= 10^{-4} \text{ m}^2/\text{s} \\ 1 \text{ ft}^2/\text{h} &= 0.258\,06 \text{ cm}^2/\text{s} \end{aligned}$$

Other ways of measuring and reporting viscosities have been used which depend on timing the flow of liquid from one vessel to another through a small orifice or short capillary. Such devices were developed empirically, and although they were convenient to use and could give results even on viscous liquids in a short time, they were not amenable to mathematical analysis and were only capable of yielding relative viscosities. Conversion of efflux times from such instruments as the Redwood, Saybolt, or Engler into dynamic or kinematic viscosities is only possible by complicated and inaccurate correlations which are not recommended. The use of such instruments is fast disappearing, although reference to them, and particularly to viscosities expressed in terms of Redwood seconds, Saybolt seconds, and Engler degrees is still found in the literature.

Temperature has a marked effect on viscosity. The effect is different for liquids and gases. With gases the effect of a temperature increase is to increase the viscosity; with liquids however, the effect is to reduce the viscosity. The temperature relationship, although not well understood, is of great importance in connection with lubrication since as a lubricating oil heats up in use the viscosity decreases, and this may render the oil useless for its purpose. An indication of how temperature affects viscosity is given by the Viscosity Index, an empirical number which effectively compares values of viscosity at two different temperatures. In recent years, by the addition of suitable additives, lubricating oils with remarkably flat viscosity-temperature gradients have been developed. These oils possess a suitably low viscosity at start-up to enable satisfactory flow and lubrication, and still possess a sufficiently high viscosity at high working temperatures to maintain a safe oil film.

Pressure also has some effect on the viscosity of oils, a pressure of approximately 7 MN/m^2 (about 1000 psi) will increase the viscosity by about 15 per cent.

Viscosity is important as a measure of the resistance to flow of a fluid, and hence in the calculation of power requirements to move fluids from one part of a system to another. Its importance in lubrication problems is discussed above. When combined with other properties such as density, it can be used to give valuable information concerning the composition of petroleum fractions; for example the Viscosity-gravity Index was the earliest constant (1928) to be proposed for this purpose. It was based on specific gravity and Saybolt viscosity. It was of particular value for indicating a predominantly paraffinic or aromatic material. The lower the value of the index the more paraffinic the fraction. Other uses of viscosity data in ring analysis have been described in the previous section (p. 320).

Surface Tension

Surface tension (σ) (interfacial tension) is a measure of the attractive force acting at a boundary between two phases. If the phase boundary is between a solid and a fluid or between a liquid and a gas the term used is usually surface tension and if between two liquids, interfacial tension. The force is measured either in J/m^2 or N/m; the older units of erg/cm^2 or dyne/cm are equal to 10^{-3} J m^{-2} = 1 mN m^{-1}. A rise in temperature leads to a fall in surface tension and the higher the molecular weight of hydrocarbon material the higher the surface

tension. The main importance of surface tension is that it controls the ease of formation and the stability of emulsions and foams. It also governs the detergent properties of an oil. It may also, together with viscosity, control the amount of oil recoverable from a crude oil reservoir.

Specific Heat

This is normally defined as the quantity of heat required to raise unit mass of material through one degree of temperature. Thus the unit is measured in J/kg K. Such a definition in fact describes specific heat capacity, and is not related to the heat capacity of water. The more common units of Btu/lb °F or cal/g °C (which are numerically equal, being effectively the ratio of the heat required to heat the substance to that required to heat water) are related to the SI unit by 1 Btu/lb °F = 1 cal/g °C = 4.1868 kJ/kg K.

For most hydrocarbons specific heat is almost a linear function of temperature (increasing as temperature increases). It decreases, however, as the density increases.

For liquids specific heat normally implies measurements at constant (atmospheric) pressure. The value is not very dependent upon pressure, and the value given is almost identical with the value obtained at constant volume. For gases, however, the values at constant pressure and constant volume are quite different, the value at constant pressure being the greater by an amount equal to the specific gas constant.

A knowledge of the specific heat of a fraction is of importance in determining net heat fluxes in all heating and cooling problems.

Latent Heat

Phase transformations (melting and vaporization or the reverse processes, etc.) are not accompanied by a sensible heat change (rise in temperature), although they are associated with heat absorption or evolution, and these heat effects are called Latent Heats. Such changes are normally measured at constant pressure and are thus enthalpy changes, although values for the constant volume (internal energy) changes are obtainable in thermodynamic tables. The unit is J/kg (1 Btu/lb = 2.326 kJ/kg).

Heat of vaporization is perhaps the most important latent heat in petroleum engineering. It decreases as the temperature rises and becomes zero at the critical temperature (this phenomenon forming, in fact, a useful indication of the critical point). The importance of latent heat has led to many methods of obtaining such data from temperature and the more readily obtainable physical properties such as density. These correlations, although they contain a degree of empiricism, are generally based on the Clausius Clapeyron equation.

As with specific heat, values of latent heat are needed in order to calculate heat effects, particularly for distillation equipment.

Total Heat Content

This is a measure of the amount of heat in a quantity of material relative to a suitable base temperature. It is normally measured at constant pressure and

may thus be referred to as enthalpy. It is the sum of the total latent heat changes and the product of specific heats and temperatures for the system. The unit used is the same as that for latent heat (J/kg), and the uses are in the preparation of heat balances.

Critical Properties

A study of the pressure, volume, and temperature relationships of a pure component reveals a particular unique state where the properties of a liquid and vapour become indistinguishable from each other. At that state the latent heat of vaporization becomes zero and no volume change occurs when the liquid is vaporized. This state is called the critical state and the appropriate parameters of state are termed the critical pressure (P_c), critical volume (V_c), and critical temperature (T_c). It is an important characteristic of the critical state for a pure component that with values of P or T greater than either P_c or T_c the vapour and liquid states cannot coexist at equilibrium, and thus P_c and T_c represent the maximum values of P and T at which phase separation can occur.

Since the critical state of a component is unique it is perhaps not surprising that a knowledge of P_c, T_c, and V_c allows many predictions to be made concerning the physical properties of substances. These predictions are based on the Law of Corresponding States which states that substances behave in the same way when they are in the same state with reference to the critical state. The particular corresponding state is characterized by its reduced properties, i.e. $T_r = T/T_c$, $P_r = P/P_c$, $V_r = V/V_c$. The use of this concept permits generalized plots in terms of reduced properties to be drawn which are then applicable to all substances (which obey the law) and can be of great value in determining thermodynamic relationships. It is rare in petroleum engineering to have to deal with pure substances, and unfortunately the application of the Law of Corresponding States to mixtures is complicated by the fact that use of the true critical point for a mixture does not yield correct values of reduced properties for accurate prediction from generalized charts. For a mixture the critical state no longer represents the maximum temperature and pressure at which a liquid and vapour phase can coexist, and phase separation can occur under retrograde conditions.

For engineering purposes this difficulty is resolved by the use of pseudo-critical conditions, which are based on the molal average critical temperatures and pressures of the compounds of the mixture. Although use of pseudo-reduced conditions for mixtures of hydrocarbons is generally satisfactory, this is not true for states near the true critical, nor, in general, for mixtures of vapour and liquid.

PVT Relationships

Knowledge of the pressure, volume, and temperature of a system forms the basis of the calculation of the thermodynamic relationships of the system. These properties are easily measured, and since they are sufficient to define the thermodynamic state they are termed the Parameters of State. However, they are not independent, and in fact any two are sufficient to define the state of a system of known mass. A simple treatment of a mathematical model of a gas

based on kinetic theory yields a relationship $PV = nRT$, where n is the number of moles of gas and R a universal constant equal to 8.314 kJ/kmol K. This mathematical model is called the Perfect Gas, and real gases which behave in this way are called Ideal Gases. Most light petroleum gases, air, flue gases, etc. may be treated as ideal up to pressures of about 1.5 to 2 MN/m^2 (approximately 250–300 psi) provided the temperature is well above the critical. For heavier vapours and for lower temperatures a more accurate equation of state is needed. Sufficient accuracy is normally obtained for engineering purposes by the use of the compressibility coefficient (Z), where $PV = ZnRT$. The compressibility coefficient is a function of temperature, pressure, and the nature of the gas, but values can be obtained from generalized charts by use of reduced temperatures and pressures (pseudo-values in the case of mixtures).

In the calculation of PVT relationships it is often useful to use the concept of 'standard conditions' at 0°C and 1 atm (approximately 10^5 N/m^2) 1 kmol of the perfect gas occupies 22.4 m^3 (the corresponding value in British units is 359 ft^3 at 32°F and 1 atm or 379 ft^3 at 60°F and 1 atm (both values for 1 lb mole)). When using these relationships it is important that both pressure and temperature be expressed in absolute scales. Gauge pressures and °F or °C must *not* be used.

Distillation Range and Boiling Point

The temperature at which a pure component boils at atmospheric pressure is an invariable property of the substance and is in fact a useful guide to the identity of the material. Mixtures do not have a single boiling point, but they 'boil' over a range of temperature depending on pressure, composition and the nature of the apparatus used to carry out the experiment. For the very complex mixtures of hydrocarbons met with in petroleum fractions, the nature of the apparatus used is of great importance. Relatively simple apparatus which gives a general idea of the distillation range (such as that in the IP or ASTM standard method) yields very little information about the composition of the fraction, and may not give an indication of the presence of low- or high-boiling components. More sophisticated apparatus which gives a high degree of fractionation yields a 'true boiling point' curve which gives much more information, and may even, in the case of relatively simple mixtures, permit composition to be determined.

Distillation range is of value in assessing the suitability of petroleum fractions for various applications, particularly in respect to volatility. Such information is also needed for the design and control of distillation columns. It is also useful, usually in conjunction with some other physical property such as density, in characterizing petroleum fractions to permit prediction of other properties.

Vapour Pressure

At moderate pressure, the total vapour pressure of a mixture is equal to the sum of the partial vapour pressure of each component (Raoult's Law). Provided a hydrocarbon mixture obeys Raoult's law, knowledge of the composition of the liquid phase and the vapour pressure of each of the components permits the composition of the equilibrium vapour to be calculated. In practice, deviation

from Raoult's law is common, particularly at high pressures, and even at moderate pressures with the higher boiling hydrocarbons. In these cases equilibrium vapour and liquid composition may be calculated by the use of liquid–vapour equilibrium or K charts, which take such deviations into account.

Vapour pressures of petroleum fractions may be measured in several different ways. One of the most common is the Reid Method, but this does not normally give a result which agrees with the true vapour pressure as calculated from hydrocarbon analysis. This is largely due to the evaporation of light hydrocarbon vapours during the determination of Reid Vapour Pressure.

Because of its use in the calculation of equilibrium vapour liquid compositions, vapour pressure is of prime importance in the design of distillation, evaporation, and condensation equipment. It is also important in the safe design of storage vessels and any equipment subject to high pressures.

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10

The Petroleum Refinery

By D. P. PLUMMER

INTRODUCTION

The petroleum refinery is supplied with crude oil from the oilfields and sends out some or all of the wide range of petroleum products required by the market. In the early days of the industry, up to perhaps 1925, a few simple products were made: petrol, kerosine, fuel oil, lubricants, and wax. Straight distillation processes were adequate to produce them, perhaps followed by simple chemical treatments of the mixing and settling type to make them marketable. Today petroleum is the source of hundreds of products, ranging from gases, volatile liquids to bitumen and solid waxes; and it is also the source of the hydrocarbon feedstocks for the vast petrochemical industry that has grown up since the Second World War. Moreover, besides distillation, there are now several other separation processes; and there are a variety of conversion processes (see Chapters 14 and 15) that alter the chemical nature of the material and give considerable control over the quality and output of products for sale, making these less dependent upon the nature of the crude oil.

Chapter 9 shows that the composition and properties of crude oils vary considerably from one oilfield to another. Refining crude oil is the art of choosing the crude oils (so far as choice may exist) and of using the flexibility of the refinery processes available so as to make the products required for the market in the way showing the best financial return for the cost expended. It is not a fixed goal. Prices of crude oils and the required quantities, quality, and proportions of the different products vary with market demands, and with the passage of time there is persistent demand for higher quality. The refinery operation must constantly be studied to adapt to changed needs. It takes from two to four years to design and build a new unit in a refinery, whether the process itself is new or established, so the decision to adopt a new process or build more of existing types of units must be taken in anticipation of market requirements and trends.

THE OIL REFINERY

Refineries used to be built near the producing oilfields and the products almost entirely exported. Since the 1950s refineries have been located chiefly in the consuming areas of the globe, ideally choosing the crude oil and processes so as to make the product range required with the minimum need to export surpluses or to import deficits. The reasons for the change come under three headings. First, the number of products now marketed and the exacting quality required, which may vary from country to country; secondly, the lower cost of moving crude oil in the huge quantities required compared with the expense of moving finished products in much smaller individual quantities. Since 1960 it has been found economic to build very large crude oil carriers; in 1940 a very large

oil tanker carried 20 000 tonnes of crude oil, by 1950 this had risen to 70 000 tonnes, while by 1970 very large tankers carrying from 200 000 to 300 000 tonnes of crude oil were commonplace, resulting in much lower cost per tonne moved. Thirdly, there have been political and national considerations arising often from the fact that a certain country will want to have oil refining capacity of its own.

These developments in scale greatly increased the difficulty of finding a site for a new refinery. Generally the refinery receives its crude by modern very large tankers, which require very deep water (60 to 90 ft) for berthing, or by long-distance pipeline from such a deep-water crude import terminal. Society has become very demanding in its concern about pollution and public safety, and to obtain planning permission for a new refinery has been a matter of difficulties, delays, and protracted enquiries. It may be that to provide a *cordon sanitaire*, a buffer area between the new refinery and the local residents has been stipulated.

These constraints may well continue to apply where new refinery sites are sought, as in the developing countries. Due, however, to the present trend of falling energy consumption, the problem in many developed countries is the converse, as a result of programmes of both energy conservation and moves to other energy sources, such as the substitution of oil fuel by coal, natural gas, and nuclear energy. Thus, of total world refining distillation capacity estimated at sixty-six million barrels per day outside of the Communist countries, only some 65 per cent was utilized in 1981 compared with 71 per cent in 1980. In industrialized regions therefore, such as Europe, the United States, and Japan, considerable rationalizing of this surplus capacity is now a priority. This has resulted in the closure of some refineries and increased mothballing, in particular, of distillation units, with transfer of operations to others.

Development of Refineries

Refineries vary in size and complexity. A small refinery will take in 2000 to 10 000 tonnes of crude oil a day, a large one 20 000 to 60 000 tonnes. The world's largest refinery exceeds 90 000 tonnes per day. A very simple early type of refinery may make only gasoline, diesel fuel, and heavy fuel (Fig. 1).

The crude oil is distilled into gaseous hydrocarbons, which are burnt as refinery fuel, light gasoline, naphtha, diesel fuel, and heavy fuel. By choosing the crude oil, diesel fuel so made is immediately fit for use; so is the heavy fuel. The light gasoline will need sweetening, a simple chemical treatment, and is then fit for blending with other components of a higher octane level into motor gasoline.

The naphtha distillate is of very low octane number, perhaps 40, compared with a market demand of over 90. It is catalytically reformed, by which process octane numbers of 95 to 105 can be obtained. This 'reformate' is blended with the more volatile light gasoline to give gasoline of correct volatility and high octane number. To summarize, such a simple refinery would consist of a crude oil distilling unit, a gasoline sweetening unit, and a catalytic reformer. Refineries of this kind have been in operation, usually small, say 2000 to 4000 tons/day of crude oil. The flow scheme for such a simple refinery is given in Fig. 1, but most simple refineries will need to produce kerosine for the local

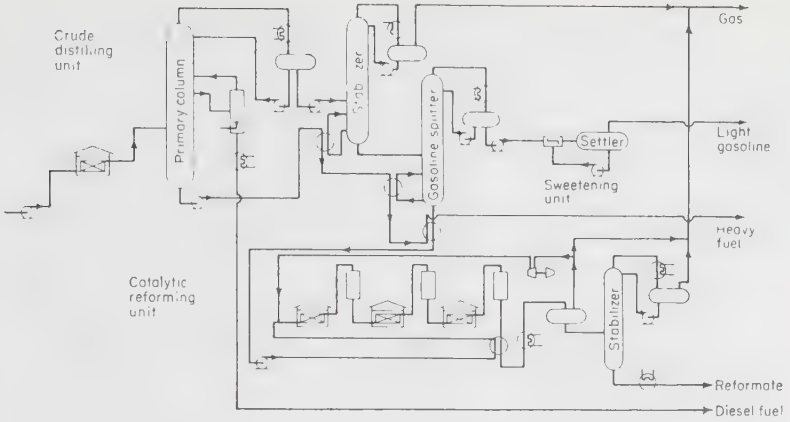

FIG. 1. Flow scheme of a very simple refinery.

market, which will require an additional draw-off from the distillation unit, and the kerosine will also need refining, at least sweetening, to make it of marketable odour.

The next stage of complexity is often to add a desulphurization unit to treat the diesel fuel. This much widens the range of crude oils available to the refinery to process, since few crude oils give suitable diesel fuel by distillation alone: this will lower the real cost of crude oil to the refinery. Usually also the growing refinery will be called upon to make liquefied petroleum gases (LPG). These stages add the desulphurization unit to the refinery, and a more elaborate distillation of the crude oil needed to make propane and butane as new streams. The kerosine may also, perhaps, need desulphurizing, unless one again restricts the choice of crude oils. The refinery flow scheme then becomes rather more complex as shown in Fig. 2.

Such a refinery is referred to as a simple 'Hydroskimming' Refinery, commonplace in many areas, e.g. in Europe up to the late 1960s to 1970s. (For this reason the 'hydroskimming' refinery scheme will be taken as the 'base case' in considering, in Chapter 11 on Future Refinery Trends, the various types of yield enhancements currently being selected in order to meet the refining demands both of the present day and for the future.)

As the need develops to produce speciality products such as bitumens, lubes, waxes, etc., and to increase the yield of premium products such as motor gasoline above that simply obtainable from crude, many more units will be added, and a large and complex refinery will have some or all of the following:

(a) Vacuum distillation to make heavy distillates suitable for catalytic cracking or hydrocracking or manufacture of lubricating oils, and a residue which may be air-blown or further distilled for bitumen.

(b) Catalytic cracking which makes gases suitable for liquefied petroleum gas, olefinic hydrocarbons, the feedstock for alkylation, and many petroleum chemicals; and cat-cracked gasoline, a high-grade gasoline blending component.

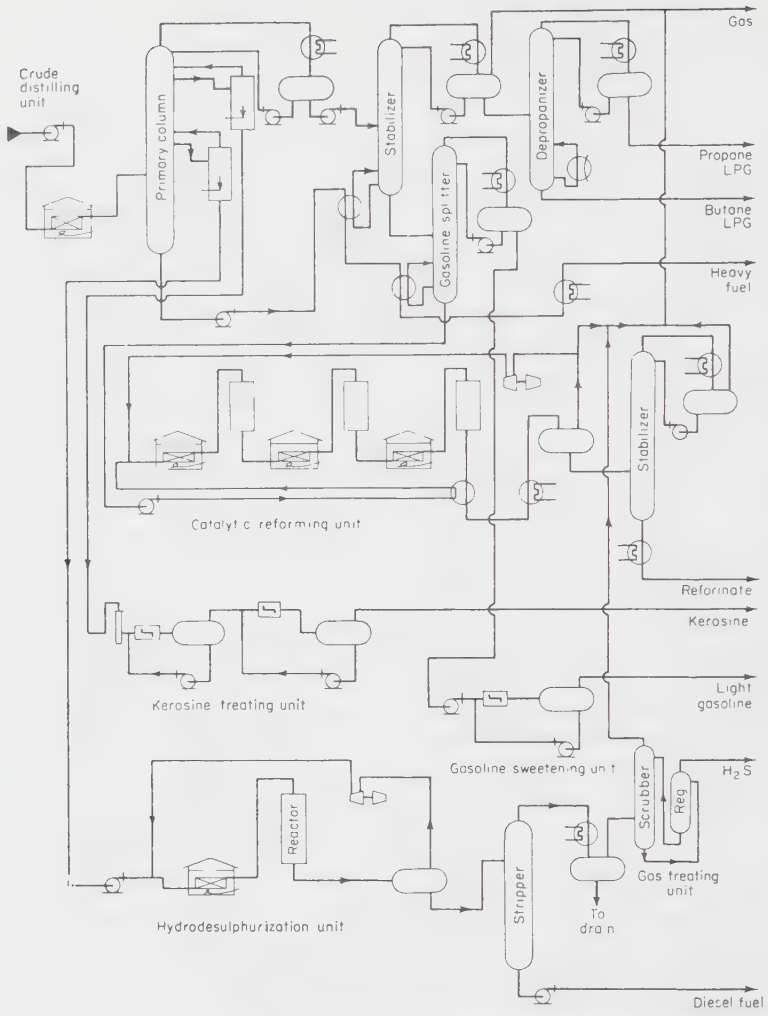

FIG. 2. Flow scheme of an integrated hydroskimming type refinery.

(c) Hydrocracking which makes additional naphtha feedstock for catalytic reforming, additional jet/diesel fuel, and a low-sulphur fuel component.
(d) Solvent extraction for kerosine refining.
(e) A lube oil extraction unit and possibly also a propane de-asphalting unit for the primary extraction of heavy distillates to make a range of lubricating oils.
(f) Dewaxing plant, to de-wax the lube oil after extraction; then de-oiling of the crude wax and final purification of the wax by hydrogenation.
(g) Alkylation unit to synthesize the very-high-octane components for gasoline out of by-product gases from processes (b), (c), and the primary distillation of the crude oil.

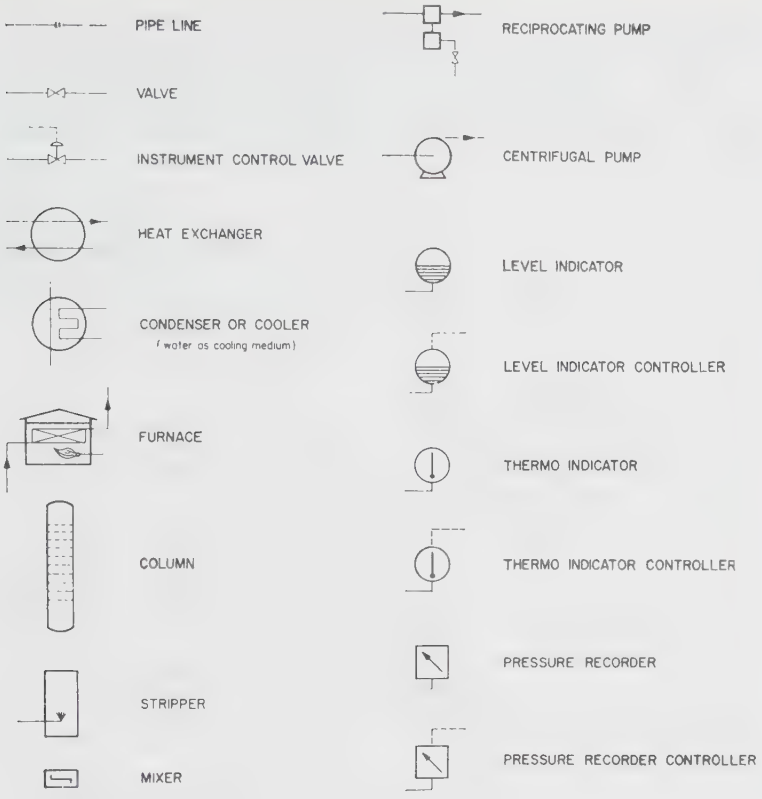

FIG. 3. Symbols used in refinery flow sheets.

(h) Sweetening and desulphurization for jet fuel.

(i) Aromatics-extraction unit to separate naphtha into its aromatics, useful as such in industry as solvents or for chemical manufacture, or for high-octane gasoline, and non-aromatics, valuable for special aviation fuels or as feedstock for petroleum chemicals, e.g. by steam cracking.

(j) Lubricating oil refining plants to remove resinous type impurities from lubricating oil stocks, and blend facilities to achieve the finished products by blending and the incorporation of additives.

(k) Visbreaking, thermal cracking, or coking plant to convert fuel oil fractions into additional gasoline and diesel range material, and reduce fuel oil yield.

It will be seen that the flow scheme of a large and complex refinery, if presented as a single diagram, would only bewilder the inexpert eye. If, as is frequent, there is an adjacent petroleum chemicals plant, with full interchange of streams as may be needed, the number of lines necessary to represent the full working of the whole integrated complex is very large indeed, and a complete diagram probably does not exist. Such a complex is perpetually under modification to accommodate new crude oils or new products or new quantities to satisfy incessant market changes, and the all-on-one-page flow scheme is not

much help to anybody. What is called a Product Flow Scheme or familiarly a block diagram is sometimes used to represent the operation of a refinery. The simple refinery of Fig. 1 then becomes the block diagram Fig. 4, and a complex refinery may be represented by Fig. 5. If there is an adjacent petrochemicals plant, fully integrated with the oil refinery, even the block diagram becomes quite a maze.

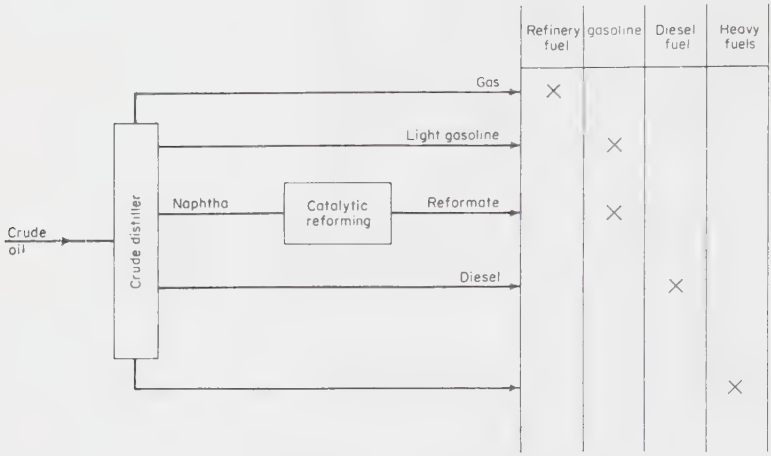

FIG. 4. Simple refinery—Block diagram.

Modern developments

The period from 1948 to 1973 was one of great growth accompanied by improvements in quality of the whole range of oil products. This led to a remarkable increase in the number of oil refineries and in the capacity of those already existing. The size of individual process units was increased dramatically, taking full advantage of economies in operating cost per tonne processed. The capacity of primary distillation units increased from 6000 tonnes/day, about the largest in 1948, to 30 000 tonnes/day by 1973; and the capacities of secondary units and conversion plant similarly increased several fold.

Since 1973 the price of crude oil has escalated far beyond any foreseen figure, and this has had a great effect on demand. The demand in terms of volume has fallen steadily, especially demand for fuel oils consumed by industry, and the completely changed economics has given the refinery every incentive to maximize the production of higher price products rather than fuel oil. This has given rise to what is called 'conversion strategy'. The demand for distillate products under present conditions grows proportionally more (or falls less) than the demand for heavy fuel, and this is expected to continue as far as the future can be foreseen. As supplies of oil become more limited or too high in cost to meet all needs, crude oil will tend to be reserved more and more for making those products which cannot readily be replaced from other energy sources. For example, transportation will continue to be based on petrol, diesel and, for

aircraft, jet fuel, while industrial furnaces and power generation will switch to other fuels such as coal (or nuclear). New plants, therefore, will be needed to process heavy fuel for the production of distillates. To date there are three main approaches.

First the visbreaking or thermal cracking route, in which conversion is by heat alone which breaks down the heavy fuel to lighter gasoline and middle distillate, with a yield reduction of fuel residue.

Secondly, there is the catalytic cracking process, involving heavy distillate conversion to cat-cracked gasoline, middle distillate, and light olefine gases which can be alkylated with isobutane. Where catalytic cracking capacity is not limited, further feed can be obtained by the removal of asphalt from fuel

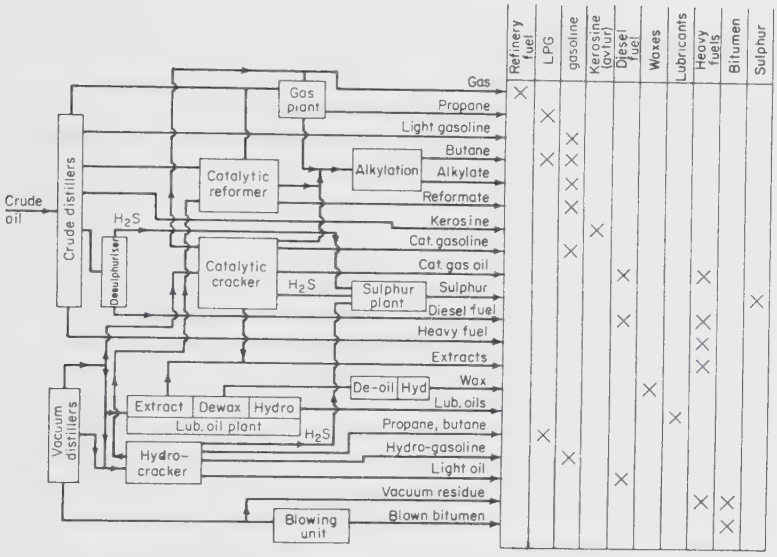

FIG. 5. Integrated refinery—Block diagram.

residues by precipitation with butane to give a larger yield of higher quality gasoline, although at added cost. Indeed, surplus cat-cracker capacity can be filled by the augmentation of distillate feed by the addition of residue crude fractions direct, although dependent upon the trace metals (V and Ni) and the asphaltene contents of the residues.

Thirdly, hydrocracking, a high-pressure hydrogenation process having the flexibility to convert fuel oil components into high value products ranging from gas, LPG, and gasoline to diesel oil or lubricating oil may be chosen.

With these processes a refinery may produce asphalt, or its equivalent in very heavy fuel oil yield, and only distillate products. The ultimate stage in the reduction of fuel can be attained by a coking process, in which fuel oil yield can be extinguished and instead a solid coke fuel product left. The various yield patterns which are attainable by these various conversion routes are illustrated in Chapter 11 on Future Refining Trends.

Operation of a Refinery

In designing a refinery or an extension to an existing one, there must be a clear idea of what it has to achieve in terms of quantity and qualities, and how any surpluses will be disposed of or deficits made good. It must be realized that from design to the first operating day is two to four years in time, that market demands never cease to change, that the availability of certain crudes will change and that new crude oils, unpredictable in quality until produced, are being discovered; so that by the time the plant operates, its feedstock and its products may differ from the ideas of the design. Large differences may require that the operating units be modified, involving loss of production while they are off-stream for this to be done. Smaller differences are accommodated in two ways. First, in a complex refinery most products are a blend of several streams and there is a certain flexibility in deciding how each refinery stream is divided amongst the outgoing products. Secondly, by adjustment of the operating conditions, temperature, pressure, residence time on catalyst, heat input to furnaces, etc. changes in the properties and proportions of the product streams from a given unit can be made. Exactly what change in the operating conditions best brings about the desired change in the product streams is partly calculable from the principles underlying the technology of the process, partly known from test run results, and partly from experience.

Having decided what temperature or what pressure is desired at a significant point in the unit, for instance the inlet line to a reactor or to a fractionating column, the operator must rely on the unit to operate to these conditions. For instance, if 502 °C is required at the inlet to the reactor of a catalytic reformer this temperature must remain steady within ± 1 °C: if it rises to 504 °C the properties of the product will alter, and perhaps also its yield. Similar steadiness would be required for the temperatures at the top and bottom of a fractionating column. This cannot be obtained by manual operation, and all refinery units rely for steady operation on controllers of flow, temperature, pressures and level, and, in blending operations, on blend-ratio controllers. These require a high degree of maintenance skill, often depending on electric circuits and carefully adjusted pneumatic valves. Such instruments usually control the variable from, and record it at, a central location, the control room in which a skilled operator can see exactly what the unit is doing and can vary plant conditions. Instrument readings are often fed directly into a computer which assists with the supervision of the process, and can in many instances make the necessary adjustments without human intervention. These control instruments are described in Chapter [34], so that mention only is made here to emphasize how dependent a modern refinery is on them. A large refinery unit, such as a 5000 tonne/day catalytic cracker, may have 150 of these control instruments, each recording on a chart or visual display in the control room.

Operation of the refinery involves not only operation of the actual units such as distilling or reforming units, but of making a daily, weekly, monthly programming schedule stating what each unit must do and how the product streams from the units will be blended to the final saleable products. This is the art of programming and scheduling, using all the resources available to meet the market demands in the most economic way. Today computers are used to state this problem in terms of a mathematical analysis. Such an analysis

requires an immense amount of data, and the result can be no more accurate than the data provided. For every refinery unit, the capacity and operating cost for every possible mode of operation and the properties of the feed and product streams must be known, and if the area being programmed has several refineries, distribution costs and marketing costs must be known, and how they vary for each refinery. The combined data are reduced to a number of equations incapable of exact solution, but it is feasible to find values of the significant variables which will involve the system in minimum cost, and to say which are the most significant variables.

Employment of computers to do this is now an accomplished practice taking advantage of their speed and memory or capacity to store data. Even when the complexity of the problem allows only trial-and-error methods of solution the computer has an overwhelming advantage. The best of two hundred trials is often far better than the best of two or three that time would allow to be done by hand, if indeed hand methods of calculation could be used at all. It is also feasible to mount the computer on the plant so that it is automatically programmed and operated for minimum cost. It is the practice to have a computer to control the final blending of product streams into the saleable products delivered to customers, since this gives very accurate control over the final blend. The use of computers is described in Chapter 34.

In any refinery it is usual to publish for management use a daily statement of how much crude oil is processed, the intake of each refinery unit and what product streams are made; also the contents of each refinery tank whether of crude oil, intermediate material, or final products. In this way it can be foreseen that tankage space is available to receive the crude shipments, and perhaps that certain products are tending to accumulate or that stocks of them are becoming low. The laboratory will also report if any stream or final product fails to meet the grade or is likely to do so, so that some remedy can be found before time and money have been wasted in having to reprocess the material. There is a tendency to do the main quality control of plant streams on the plant itself, and in the past such a process unit would have a small laboratory facility adjacent to its control room; nowadays many of the tests are done automatically by continuous monitoring devices on the unit that take a sample, test and record the result of the test either continuously or every few minutes by an automatic programmer. This is quicker and surer than sending a sample to a laboratory. For final check before despatch of saleable products, however, the laboratory is still in control.

The Auxiliary Equipment of a Refinery

The oil refinery needs heating, cooling, and power. Typical daily figures for a large refinery could be 1800 tonnes of burner fuel, 40 megawatts of electricity, and 750 000 tonnes circulation of cooling water. These needs will now be considered.

Refinery fuel system

Fuel consumption in a refinery is usually between 4 and 10 per cent of crude oil intake depending upon the complexity—see the table in Chapter 11 on Future

Refining Trends. Primary distillation of crude oil takes 1.3 to 2 per cent of fuel, but several of the secondary processes and steam raising add to this figure. This is for burner fuel used in the furnaces to heat or re-heat the oil in the various processes. These furnaces may be up to 200 million Btu/hr heat release, corresponding to 60 megawatts. The refinery will preferably burn as fuel what is not directly saleable, or unstable or waste materials and surplus gas, and will only make up with saleable fuel if necessary. The liquids are usually blended and heated to the temperature giving best viscosity for atomization and then distributed by a ring main to all refinery furnaces.

Refinery power

Pumps of 800 to 1200 hp are common in the refinery units, and the power needed by a refinery is very considerable. There are four main sources of power in use, electricity, steam, gas and diesel engines, and internal combustion turbines. Whether a refinery will purchase electricity from a national grid or a convenient supplier, or generate its own or do part each way, is a purely local decision depending on prices and the availability of capital. If the refinery depends wholly on outside supplies there must be a clear plan what to do if the supply should fail: multiple feeders from the grid can render this emergency unlikely, but it cannot be made impossible. Electric drive is usually the preferred drive for the pumps on any unit, but it has the practical limitation that there is a maximum speed for the motor of 3000 rev/min for 50 cycle ac and so on. For multi-stage centrifugal pumps and large compressors higher speeds give a more compact unit and a greater efficiency, 5000 to 12 000 rev/min being the preferred range, and steam turbines are in use for this range. There is also the view that steam can be a more reliable source of power for critical drives, sudden failure of which might be dangerous or very costly. So every refinery unit has a steam and an electricity supply. The steam supply network to a refinery can grow into great complexity unless it is carefully designed and reviewed: it is important that there is always flow in all sections that are in use, and great care must be exercised to trap out steam condensate so that it is not carried forward into high-speed machinery. A refinery near to a gas field or to a gas supply that is cheap would use this as fuel in gas engines as an alternative to steam or electricity. In remote parts of a large refinery, to obviate a long steam line or electric cable, the diesel engine or internal combustion turbine would be considered in spite of somewhat higher maintenance cost. Private generation of electricity by internal combustion turbines running on surplus streams can be attractive. Steam is a heating medium as well as power for a prime mover in the refinery, especially where an unfired unit is dictated by safety considerations. In many refineries HP steam is generated at 1500 lb/in^2, run through turbines to generate electricity, and exhausted at 250 psig for the supply to the refinery; the refinery exhausts at 50 psig and this is the heating or process steam. Such generators should be 20 megawatts at least, and then if the supply of 250 psig and 50 psig steam meets demand the scheme is often attractive. Each refinery is a special case in deciding how the various forms of power will contribute to meet the total power demand. The decision is, however, very important since a real mistake can be costly and well nigh impossible to rectify.

Refinery cooling

Before 1955 it was rare not to use water for cooling, either fresh water recycled over cooling towers or sea or saline water pumped once-through. A once-through saline supply means cheaper water and usually colder water, but needs corrosion-resistant tubes in the condensers, about doubling their cost. Air cooling is now the favourite to replace or minimize the need for water cooling. More surface is needed in the condenser, a fan is needed to increase the air velocity, location of the condenser can be a problem, and usually there is higher first cost. Once fitted, however, air coolers cost very little to run and are, save for sudden and gross leakage, immune from failure. If the fan fails the duty falls to about half, which is usually quite enough for safety; and the elaborate routine for total cooling water failure can be forgotten.

Other auxiliary equipment

Compressed air is used for driving pneumatic tools, chemical oxidation and regeneration processes, and the automatic control valves of the plant, many of which are air-operated. There may be a refinery air main or the supply may be by local compression. For further discussion of refinery utilities the IP Refining Code 1981 may be referred to.

Jetties, rail and road delivery and receiving facilities, warehouses, engineering workshops, storekeepers' yards, laboratories, first aid and medical officers' quarters, general and local offices must all be built as part of the refinery.

The cost of tankage for crude oil and products is very high and oil stored in tanks represents a huge sum of money. Hence it is important to have the right number of tanks of the right capacities, and to hold no more oil in inventory than is necessary. Tankage for crude oil is dictated by the size of ship's cargo, the reliability of supply, the throughputs of the distillation units, the number of crude oils that must be separated, and sometimes by government guidance on what is a prudent reserve for the country. If crude oil is received by pipeline less tankage suffices, the tanks at the input end of the line being in a sense common storage for all recipients. Tanks up to 100 000 m^3 capacity (about 250 ft diameter and 72 ft high) are now common for crude service. For product tankage, the difficult decision on how much to store must take into account the storage available in the marketing installations, as well as the various modes of distribution to them. In this way an optimum storage-plus-distribution cost can be realized. For crude oils the contents of the tank can generally change from one crude oil to another, always remembering that in normal use an empty tank may still contain a 'bottom' of up to 5 or 10 per cent. For product tanks white oil products (e.g. gasoline) must be kept separate from dark (e.g. diesel fuel) or black (heavy fuel), though some interchange in use may be permissible, particularly after cleaning. The pipelines serving the tanks dictate how they may be used, and the design and operation of pipeline systems require careful planning. Large sums of money can be saved by laborious and patient study of what the requirements and flexibility are and are likely to be. The main pipeline runs for a large refinery may total up to several hundred miles. The rate at which the modern very large crude tanker discharges crude oil often requires 48-inch diameter lines to the main crude oil tankage. Tanks are

gauged by hand dipping with a graduated steel tape wetted to the level of the oil, or by automatic devices consisting of a level sensor and a means of registering its height above the tank bottom. These automatic devices can be made to read out at a distance, perhaps all in a central control room, by electrical means. More detail may be found in Part V, 'Automatic Tank Gauging' of the IP *Petroleum Measurement Manual*. A modern development is to feed these readings directly to a computer which monitors the tank operations and assists in making decisions on blending or moving of stocks from one tank to another. All tanks must have provision to drain water from the lowest level; in some situations water is occasionally used to wash out pipeline systems unless there is special reason to avoid it, rain may enter via the roof seals of a tank, and water is always present in crude oil. The residence time in the tank provides an opportunity for the water to settle out, and drawing off water is part of tank farm operation. This water is oily as a rule and must be sent to oil interceptor equipment as described later. The rule is to have the smallest possible number of connections to the tank, which means the fewest valves to check over and maintain. One water drain, one low-point oil drain, and one main in-and-out connection are normally all that are needed below the tank liquid level. The normal shape for bulk oil tanks is an upright cylinder with the roof either fixed (the cone roof tank), or floating on the tank contents. If the tank diameter exceeds 120 ft it is usual to avoid the girder work needed to support a fixed roof, and to adopt the floating roof. These tanks will not stand internal vapour pressure greater than that of stabilized crude or gasolines. For petroleum products of high vapour pressure, such as liquid butane or propane, the tank is made truly spherical and supported on legs welded to the shell. A sphere requires the thinnest plate for a given internal pressure. For moderate pressures, 5 to 15 psig, very large tanks have been made spheroidal or sessile in form, with all the shell in uniform tension as is characteristic of the sphere, but with lower height to diameter ratio. Chapter 33 will describe tanks and tankage installations in more detail.

Refinery Maintenance

All moving parts are subject to wear and this is mitigated by lubrication. Most large refineries have on the staff a specialist in lubrication who will direct what lubricant is used in each machine and study the special problems, for instance lubrication of valves and cocks that must operate at high temperature; he will also supervise the consumption of lubricants and keep their variety down to the lowest economic number, and properly report his findings. In any refinery unit certain pumps will be designated as critical, that is the unit must be immediately taken off stream if these pumps fail. These pumps will be provided with spares and automatic starters to bring them in immediately if the operating pump fails for any reason to deliver the quantity and pressure required. These decisions are part of the plant design and add to the capital cost of the unit.

These are fundamental safeguards, but refinery equipment deteriorates much more quickly and suddenly than as the result solely of physical wear. Refinery maintenance also demands a close study of chemical corrosion. It is for this reason much more than the nature of the processes used that the refiner

needs a good knowledge of the related chemistry. The effects of corrosive soil are most important for tank bottoms and pipelines, and can be much reduced by cathodic protection, the application of a small negative potential to the metal to counteract the tendency to lose metal ions. For atmospheric and soil corrosion protective coatings, paint, galvanizing (where appropriate) and so on are commonly used. Cooling water is often corrosive, especially if brackish or sea water is used; where velocity is high, metals resistant to salt water such as bronze or aluminium brass are used, and the main pipelines are coated internally with a bituminous or cement layer.

Refinery processes also use chemicals known to be corrosive such as sulphuric acid, hydrofluoric acid, hydrogen chloride, caustic soda, and ammonia. These are known materials and it is very much a matter of following known procedures. For instance, sulphuric acid at rest and cool, as in a tank, does not attack mild steel above 70 per cent acid, and if it is in motion, attack is very slow above about 85 per cent. There must be adequate safeguards against dilution, even local and temporary, below these figures, otherwise very expensive alloys are needed. For evaporating water from dilute sulphuric acid to re-concentrate it for re-use, steam-heated tubes of tantalum are often used. Caustic soda, when above 90°C, attacks stressed mild steel (so-called caustic embrittlement), and stress relieving or the use of special steels is essential. Water itself under the severe conditions in a 1500 psig steam boiler is very corrosive unless purified to rid it of dissolved oxygen and acidic substances.

These are known effects. The difficult problems of corrosion arise from the crude oils themselves under the conditions of the processes employed. It would be simple if all crude oils were only mixtures of hydrocarbons. Basically they are that, but they contain also small amounts of other substances, water and what may be dissolved in the water coming with the oil from the well, acidic substances such as fatty and naphthenic acids, compounds of nitrogen, dissolved oxygen, and sometimes particles of sand which have a scouring effect on what might have been protective films or layers on the metal walls. No two crude oils contain the same proportions or total number of these impurities, and a plant made safe by patient study for one crude oil must be studied all over again when the crude oil feed changes. Cold crude oil as received into the refinery tankage is not corrosive, except for the water layer that may settle from it. As soon as it is heated there is often enough naphthenic acid in the oil to react with sodium or magnesium chloride carried in with the water to form hydrogen chloride. This gas passes to the condensers where it finds enough water to form hydrochloric acid. The safeguard is to control the acidity of the water in the condenser or its receiver by adding soda, perhaps under automatic pH control, and/or to remove as much soluble chlorides from the oil as possible by desalting (see below). At high temperatures the naphthenic acids themselves attack the steel of the plant lines and columns. This attack can be aggravated if the crude oil contains also certain sulphur compounds; the remedy is use of corrosion-resistant alloys (such as 18 per cent Cr, 8 per cent Ni, 3 per cent Mo steel), but they are expensive, and some are very hard to form and work compared with mild steel. In many cases the primary impurity in the oil is not particularly corrosive, but decomposes when the oil is heated to give products that are. This is particularly true of sulphur compounds. The large organic sulphur molecules in the heavy part of crude oil are not very reactive, but on heating they form

hydrogen sulphide, mercaptans and, if there is dissolved oxygen, sulphur acids, all of which are very destructive reagents. Thus, above 300°C the sulphur compounds in the crude oil will attack steel, especially at places where there is rapid flow of oil (e.g. transfer lines from heater outlets). The corrosive impurities in the crude oil distribute themselves over the products of distillation. Some refineries treat all crude oil before distillation with some chemical that will take up all free oxygen, and claim that this much reduces corrosion. Also it is usually found that desalting the crude oil to levels of below 10 ppm of salt reduces corrosion of crude distillers.

Secondary processing units are also subject to corrosion because the primary products from the distillation of crude oil contain traces of materials that decompose under the process conditions to give corrosive agents. Besides the internal corrosion, the tubes of refinery furnaces, the furnace stack and its refractory are all subject to attack from the products of combustion formed at the burners. This is often severe in refineries where unsaleable sludges and by-products of various kinds are consumed in the refinery fuel, and high heat recovery is attempted which extracts so much heat from the combustion gases that the temperature falls below the critical acid dewpoint level.

Though not corrosion as such, operation of some refinery units can be severely hampered by the plugging of the lines with solid material. This solid material is commonly a product of corrosion, often finely divided iron sulphide, or it may be salt that has come out of hot crude oil because the water which held it has evaporated; or it may be a by-product of reaction, as when hydrogen reacts with nitrogen impurities to make ammonia and some acid is present to give an ammonium salt insoluble in oil. A further example is coke which can occur in furnace tubes at local hot spots where the oil is overheated. The cause of plugging is often found from a chemical analysis of the solid plug, and the plug is removed by hot water washing or, if it is very stubborn, by drilling it out, using a compressed air turbine to drive the drill. The unit must be shut down or the plugged part isolated for this work, involving troublesome loss of plant capacity. If plugging is regarded as typical of the process, the plant can be set up for periodical chemical cleaning by making provision for isolating certain sections without shutting down the whole plant and providing branches (normally blanked off) for the necessary connections. This is now a well established technique which may use strong acid, hydrochloric or sulphuric acid, inhibited in various ways to prevent attack on steel, and often containing detergents and special chemicals for the job. Used with great attention to the facts of chemistry, chemical cleaning has had great successes and can be reduced to a common routine. Unwise or improperly studied application, however, can cause serious damage and metal loss by preventing proper action of the inhibitors. Chemical cleaning is especially necessary for the tubes of heat transfer equipment where a thin film of solid deposit can reduce the rate of heat transfer to half or much less, and make proper heat exchange or temperature control impossible (see Chapter 12). Also in mass transfer equipment, extractors or fractionating columns, the size of orifices and width of clearances can become reduced by build-up of deposits and the performance of the equipment impaired long before actual blockage would occur.

Preventive maintenance is the rule in refineries since the risk in operating equipment to the point of failure or rupture is too great. It can be practised so

well as to avoid unpredicted shut-down of the units. The unit is shut down annually or every two or even three years. At the shut-down, repairs and replacements are executed to make the unit safe till the next shut-down. To this end the wall thickness of equipment is measured at a great number of places known by experience to be critical, and the rate of wastage is established. If it is too great, a different metal or alloy is used at the next shut-down. Non-destructive methods of measuring thickness of plate must be used while the plant is operating. These are based on the reflection of ultrasonic waves. Absorption of X-rays or rays from radioactive isotopes is used to detect incipient decay or cracks in welds, or in some cases to show malfunctioning of valves or moving parts. In this way warning of a repair job at the next shut-down can be given in the knowledge of the true state and strength of what is in use. Of course after repair or inspection the plant is hydraulically tested for pressure tightness in the usual way.

Refineries vary in the extent to which repair and construction of equipment or replacement of parts is done in the refinery fitting shop. It is very much a question of location and what facilities are offered by nearby contractors. Some refineries put all their maintenance work out to contractors, who employ men skilled in refinery work and conversant with refinery safety discipline.

Refinery By-products and Waste

The waste and by-products of a refinery are very small in quantity. A refinery taking in 25 000 tonnes/day of crude oil would have perhaps 3 to 30 tonnes of by-products per day to market or dispose of; refinery coke made in coking units is not a by-product. The by-products may include:

Acid sludge, resulting from treatment of kerosine, naphtha or lubricating oil stocks with sulphuric acid. It contains 30 to 55 per cent hydrocarbons and the rest sulphonic and sulphuric acids. It may be sold to sulphuric acid manufacturers or fertilizer manufacturers (for ammonium sulphate). If a customer cannot be found it must be separated into oil and an aqueous acid layer, and re-concentrated or burnt in a sulphuric acid plant in the refinery. Refiners do not like handling such acid sludge, and as disposal is a problem, acid treatment is increasingly being replaced by hydrogenation as a refining treatment, using hydrogen available from catalytic reforming.

Spent soda, resulting from soda washing of light oils may contain phenols making it attractive to a purchaser. Likewise, spent doctor solution will be rich in thiosulphates.

Spent catalysts. Valuable catalysts containing platinum or palladium are sent to the metal refiners for metal recovery as part of the supply contract. Less valuable metals, cobalt, molybdenum, nickel, are also recovered by purchasers of spent catalysts.

Naphthenic acids often accumulate in the 200°–330°C fractions from primary distillation, and can be worth recovery by soda washing and springing with sulphuric acid. The refinery does this and often vacuum distils the final acid into carefully purified grades of acid offered for sale. The acid is bought for making copper, cobalt, or chromium naphthenates, used as fungicides or as catalysts to accelerate the drying of paints.

Refinery Hazards and Dangers

Crude oil and most of its products are combustible, giving rise to the hazard of fire and explosion. Intoxication from inhaling a concentration of light hydrocarbon gas or vapour is a further hazard to be prevented. The oil industry has an excellent safety record because it has always been very conscious of these risks. In the design and layout of refinery plant and when planning its operation, safety is an overriding consideration; very large sums are spent to reduce these hazards to the minimum. Most countries have legislation to control the handling and storage of petroleum and its products, and codes of safe practice have been produced by the Institute of Petroleum in the UK and the American Petroleum Institute and similar bodies in other countries. These are used to guide the designers and constructors of refinery plant and facilities, and no piece of equipment or plant is put into operation unless it has been made safe. For details of design principles, layout, and safe operation the IP Refining Code, Part 3 (1981) should be consulted. (See also Chapter 32.

Legislation for health and safety, particularly since the Flixborough, UK, chemical plant disaster of 1974, has become stricter for standards and safeguards. It has been usual, and under recent UK legislation* is required, that an analysis be made of likely hazards for plants which are above a specified inventory level, with quite detailed calculations of what the attendant risks are to the employees and to the public. This is especially important if authorization is sought to use a new site for operation of plant or to change the process on an existing one.

Fire

Each new process brings with it its safety requirements and is given special study. The amount of oil, especially hot oil, actually being processed on the plant area is kept to the minimum. A distillation unit may process 15 000 tonnes of crude oil/day, yet contain at any one moment a working content of only 100–200 tonnes, and of this perhaps only 40 tonnes at elevated temperatures. Processing units are also arranged to drop out or handle their entire content safely in case of emergency, and this procedure can be automatically controlled by hydraulically-operated valves. Once a fire occurs the operators have initial recourse to high-pressure steam hoses or hand-held fire extinguishers of appropriate type placed at convenient points of the plant and directed by hand to smother a small fire and keep it out, very hot oil from a small leakage being spontaneously inflammable. Very often such prompt 'first aid' action will ensure that a small incident does not escalate. If the emergency grows, or is greater to start with, the fire brigade is called. A refinery usually maintains its own brigade, who know the refinery, its resources and emergencies, and have additional back-up arrangements with the local or municipal brigade. For a tank fire or large plant fire, the refinery has its own high-pressure fire main system, and water in the form of spray or fog is used more to protect the nearby equipment from the heat of the conflagration.

* The 'Notification of Installations Handling Hazardous Substances Regulations 1982', S.I. No. 1357. HMSO, which came into force on January 1, 1983, and is compatible with the similar EEC so-called 'Seveso' Directive on major industrial hazards.

Special foam-generating compounds are used to blanket the surface of burning oil from access of air, and every effort is made to pump out the oil or drain it away from the burning area. On refinery plant, a fire lasting 20 minutes is a long one, and the heat evolved may by then have done extensive damage. Tankage of the fixed roof type is more difficult to extinguish and may burn for hours, so much effort is needed to prevent the fire spreading, for example by cooling adjacent tanks or plant by water spray or fog curtain. Fires on floating roof tanks are usually 'rim fires', confined to the annular seal area between the roof and the tank shell, and are usually fairly easily extinguished by foam application to this area (see section on tankage in Chapter 33 on the Petroleum Installation). When the number of oil refineries and the huge quantities of oil processed are considered, serious refinery fires can be described as rare.

Explosion

Explosion, which can take place when a mixture of flammable vapours or gas occurs with air in the appropriate proportions between the 'upper' and the 'lower' flammable or explosive limits* and encounters a spark, flame, or other ignition source, fortunately is even more rare than fire. Plants which process the lighter hydrocarbons, LPG, gasoline, and so on, and especially hydrogen, the explosive limits of which with air are very wide, are designed and laid out with constant reference to this danger; if the hydrocarbon can possibly leak into air there must be no possible source of ignition. All plants that handle or produce hydrocarbon or inflammable gas must be arranged to vent it safely in emergency. This usually means conducting the gas to a flare, usually a pipe in a remote area extending 150 to 300 ft or more above the ground, with means to ignite the gas, otherwise it may drift back and ignite beyond control. The flare must be sited with knowledge that the full gas flow may create a flame of 200 ft length for the short duration of the release.

The infrequency of fire and explosion incidents in a well-run refining industry is well illustrated in the epidemiological survey discussed in Chapter 37 on Occupational Health in the Petroleum Industry. This survey carried out on eight UK refineries, which between the years 1950 to 1975 had some 35 000 employees, showed that for this twenty-five year period there were twelve deaths by accidental fire and explosion (of which one occurred outside of work). The figure for comparison for deaths in ordinary motor traffic accidents on the roads for this same study population in the same period was 110.

For such a record to be achieved, the highest standards of design, operational safety, and maintenance are necessary. To aid in this, petroleum streams and products are classified for their volatility into various 'classes' (Class O, I, II, III, and Unclassified) in accordance with their flashpoint, as outlined in Chapter 32, The Classification of Petroleum for Safety Purposes.

This classification is utilized in codes of practice to recommend safe criteria for design, safety distances, good operational practice, maintenance, and work control procedures, etc., as appropriate to each class. For specific details

* For a definition of 'flammable or explosive limits', since the two terms are synonymous, see Chapter 32.

reference should be made to the Institute of Petroleum's 'Refining Safety Code, 1981 (Part 3 of the IP Model Code of Safe Practice)', and to Chapter 32.

Intoxication by inhalation of petroleum vapours

Intoxication which may ultimately lead to unconsciousness and asphyxiation due to inhalation of hydrocarbon vapours is a further hazard to be prevented by high standards of plant design and practice, and in all cases (e.g. where vessels or tanks have to be entered) it is necessary to provide a safe working atmosphere by appropriate purging and testing of the atmosphere prior to issuing a safe working permit.

Exposure to hydrogen sulphide produced in many process unit streams is also one of the major hazards to be guarded against in view of its highly toxic nature. Sour crudes received at a refinery can liberate appreciable amounts of hydrogen sulphide and, if inhaled, this is lethal even in low concentrations. A number of both liquid and gas process streams, e.g. crude still, catalytic cracker and gas fractionator overhead and reflux streams, hydrotreater recycle gas streams, etc. also have significant H_2S contents.

Precautions against these exposures to H_2S and hydrocarbon vapours are given in the IP Refining Safety Code, and are dealt with in this volume in Chapter 37 on Occupational Health in the Petroleum Industry.

THE ENVIRONMENT AND POLLUTION

The refinery will discharge certain materials into the air and into adjacent drainage, rivers or sea; and now that many refineries are in or close to populous areas, often together with many other industries, great attention is paid to preventing pollution of air, ground, or water. In general oil companies have always paid great attention to this as part of good operating practice, and most countries have legislation which puts limits to tolerable discharge levels. In recent years increased public awareness has made it essential to reduce as far as can be the effect of refinery operations on the environment, and noise, not always previously regarded as a category of pollution, is now given equal attention.

Atmospheric Pollution

A principal control is that on sulphur dioxide arising in the combustion of refinery fuels which may be both gas and residual streams. The great attention paid to the thermal efficiency of modern plant tends to keep fuel consumption down, so that sulphur dioxide emission has not necessarily grown in proportion to refinery intake, but each fuel type and its contribution to overall emission must be considered. Where refinery gas containing H_2S is burnt it is usually treated for sulphur removal before combustion. There is usually local legislation giving limits for ground-level concentration of sulphur dioxide or a limit to the total sulphur emission. In some locations this may mean placing limits on the sulphur content of the fuel. Usually the requirements are met by the use of very high chimney stacks to ensure enough dispersion of the pollutants before they reach the ground. The ground-level concentration of

sulphur dioxide would be monitored by sampling at locations an appropriate distance from the refinery perimeter. These chimney stacks must often be very tall, 400 to 600 ft high, and their high cost (besides the fact that a wide chimney can be made self-supporting) has led to departure from the practice of each furnace having its own stack and to connecting the furnaces of a whole complex of plant to one huge chimney stack. This needs long and carefully designed flue ducting from furnace to stack, so arranged that any furnace can be safely shut down for maintenance work.

Other airborne emissions that are controlled include particulates, both as airborne ash from combustion and catalytic crackers, and sometimes carbon monoxide. In the UK, SO_2 and particulate matter levels, etc. are laid down for refineries by the *Notes on Best Practicable Means for Petroleum Works*, published by the Alkali and Clean Air Inspectorate. Refinery crude stabilization, cracking, and hydrotreating processes can produce large quantities of hydrogen sulphide. It is a poisonous gas of very evil smell, even at low non-toxic concentrations, and great care is exercised to prevent its leakage or discharge since not only public relations, but above acceptable threshold levels, the safety of refinery workers is involved. The practice is to treat requisite gas streams in a regenerable treating column, sending the hydrogen sulphide to a Claus unit which converts it to solid (or molten) sulphur for sale. Conversion overall can be up to 95–96 per cent as sulphur and the remainder is burnt to sulphur dioxide. A significant proportion of the world's sulphur demand is met from petroleum sources in this way.

Liquefied Petroleum Gas (LPG) is kept in enclosed pressure systems, but emission of hydrocarbon gas or vapour can arise from storage and transfer of volatile liquids such as crude oil or gasoline. It is kept low by the use of tanks fitted with floating roofs, internal floating blankets, or in appropriate cases, the fitting of pressure and vacuum valves on the vents of fixed roof tanks (see tankage description in Chapter 33 on the Petroleum Installation).

Relief valves fitted to the pressure vessels are piped up to discharge to the refinery flare. This flare is kept alight at all times so as to combust effluent gas or vapour safely, as well as being ready to deal with the more massive flow of hydrocarbons that can be released in emergency.

Water Pollution

Water effluent from a refinery can be cooling water, ship's ballast water, water separated from crude oil, steam condensate and boiler blow-down, spent chemical solutions, and the rain water that falls on the area. If the refinery is built inland or on a clean river management of all this water is a difficult problem. Replacement of cooling water by air cooling, careful segregation of clean from polluting effluent, and recycling of what might have been effluent are all primary considerations. Polluting effluent must then be treated to remove the unwanted substances. In almost every location there will be local legislation or specifications to be met. There will be maximum allowed concentrations for oil, phenols, sulphides and ammonia, and often a limit set to temperature, biological oxygen demand (BOD), and acidity. Present practice can be summed up in three categories:

(a) Primary treatment. This is always applied to any water effluent which

does or could contain oil. The object is to allow the oil drops to rise in what is called an interceptor and form an oil layer which can be skimmed off. The design aims at trapping all globules larger than 0.1 mm diameter resulting in oil contents below 25 ppm for the effluent. Originally large rectangular excavated ponds or separators lined with concrete, of a size to allow settling time and placid flow of the water (below 1 ft/min), were used. The more modern form is an enclosed tank containing inclined parallel corrugated plates spaced 1 to 2 inches apart. The oil has then to travel only this distance to form a film which runs down the surface of the plate, the residence time needed is less, and the whole installation can be made very much smaller than the old excavations; being totally enclosed it is not itself a source of malodour. Any aqueous effluent known to contain bad smelling volatile material is first run to a steam stripping column for removal of the noxious compound.

(b) Secondary treatment. The effluent from the interceptor will contain droplets of oil below 0.1 mm, as well as emulsified and dissolved oil; if the total of this is not low enough, techniques of filtration or flocculation must be employed. For flocculation, the water effluent is mixed with chemicals making a voluminous, gelatinous precipitate, usually of alumina or iron hydroxide. This precipitate, or so-called floc, carries all suspended oil, even colloidal, with it if conditions are right, and is removed in thickeners. Its disposal can be a problem. The water may also need reduction of its BOD by bio-treatment using activated sludge. It may be that the BOD reduction process also reduces the oil content, in which case the flocculation step is not needed. The plants resemble those used for the treatment of sewage.

(c) Tertiary treatment. This is likely only in inland refineries. Large holding basins are provided to allow additional bio-degradation to take place before the water is discharged or re-used. This arrangement also is a safeguard against failure of primary or secondary treatment.

Land Pollution

Increasing attention is given to the disposal of waste by dumping on land. There are now very stringent regulations, and it is often usual to dispose of solid wastes, chiefly sludges, by incineration to harmless ash before dumping or use as fill.

Noise

It is now normal for new equipment, for instance turbines or compressors, to be supplied against a maximum permissible noise level in the specification. There is a UK Code of Practice, 'A Guide to Noise-control Design in the Oil and Petrochemical Industries', published by the Oil Companies' Materials Association in three parts, publication numbers NWG 1 to 3 (available from Heyden and Son Ltd), and new general legislation is being prepared, chiefly to protect workers who may be exposed to potentially damaging noise. In some localities complaints arise from neighbouring residents of noise from a refinery, and this is an additional incentive to limit noise.

REFINERY STAFF

An oil refinery covers a large area, the units being well spaced out for safety reasons. Visitors to a refinery have always commented on the high degree of automation and the small number of workers that are to be seen. This was true even in the years after the Second World War, 1948–63, when several refineries became very large and employed up to 5000 people. In those days it was still traditional for a refinery to be self-sufficient with its own laboratories, stores, supply of spares, workshops, maintenance organization, fire brigade, and security forces, although in industrially developed locations some use was made of contractors. Even today there are areas of the world where the refinery is the first step in industrial development and must provide the full range of ancillary services. This may include dwelling houses, recreational facilities, schools, and medical services, so that building a refinery in such a location involves building what is a small town. With increasing industrial development throughout the world these locations are decreasing in number.

From that time until the present, highly competitive conditions in the economics of refining oil, and soaring costs both for material and all forms of manpower, have brought in the present 'stream-lining' phase, which is one that will persist. Staffing levels and the organization of a refinery dictate the total number of persons involved; this number must conform with the economic environment which exists at the time. By 'stream-lining' is meant using the whole range of developments in automation and control. These allow many refinery operations to be carried out with very little human aid. The whole process is often under continuous control by computers operating automatic valves with complex electrical circuits for the automatic reporting of plant data to the computer and, by the use of closed-circuit television, for making details available to a central control room. These advances have been made easier to incorporate into refineries built or extended since 1970, so that quite large refineries now operate in suitable locations with a labour force as small as 250. In an area where industrial activity is well developed, a refinery would today rely on outside contractors rather than its own employees for much of its maintenance, security, transport and construction work, and other ancillary services.

Present-day conditions of size, cost, and technical complexity call for refinery operators with a high level of education, exceeding what was acceptable thirty years ago. Recruits must have good basic education, with mathematics and some science subject, and must undergo training on the site in refinery operations and plant control. There is normally a refinery training department, and it will make full use of any accessible technical college courses that may be helpful. Training in emergency procedures is an important part of the special instruction provided by the training department. It must be remembered that the refinery plant runs day and night continuously, a plant costing millions of pounds and perhaps critical to the operation of the whole refinery being in the nightly care of a shift, which in present-day conditions may be only four men. Real emergency is infrequent and of course the skilled operator can often foresee and prevent it or give timely warning; but it is essential that the plant operator knows what to do and what he really is doing, so that he remains without panic and in control. The infrequency of the real

emergency gives limited opportunity for gaining live experience, but in many instances a process simulator, similar to those used in training aircraft pilots, can be devised, which puts the recruit in a replica of the emergency, so that his behaviour can be studied and corrected.

The refinery staff will include many technicians and fully qualified graduates, and the number will be greater if the technical department is responsible for new development work and design of modifications to the plant and services. In any event the technical department is responsible for the assessment of plant performance and capacity, and the day-to-day trouble shooting. Design of major new units is almost always done by outside firms in collaboration with the head office technical staff, but it will be the refinery technical and engineering force who have to advise on how best to fit the new piece in.

The role of the technical staff has changed over the years. Not long ago the major objective of a refinery was the technical perfection of its process operation with high on-stream time, minimum operating cost per ton and top quality products. These are still the first considerations, but they have to be brought into the total business economics of the oil company. The refinery is less a separate economic unit and much more a step in the economic journey from oil well to market-place. The decisions in the refinery can affect many other costs facing the oil company. Many refineries have a supply and economics department which plans the operating schedules and monitors the economic performance of the refinery in terms of product values; it also cooperates with the head office in long-range planning. This involves a good understanding, not only of the refinery processes and their capabilities, but of the costs and prices of crude oils and products. Close integration with the marketing side of the company is essential, resulting in a business-oriented outlook in the technical staff so that properly balanced day-to-day decisions are made.

11

Future Refining Trends

By P. JONES

CHAPTER 10 on the Petroleum Refinery listed the many conversion processes, and speciality process plants, that can be used to meet the manufacturing requirements of a refinery, ranging from the very simple to the most complex, and a further detailed description of these processes is given in ensuing chapters.

The production of the more speciality products (solvents, waxes, lubricants, etc.) is a function of the individual company's marketing needs, planning, and assessment of the economics involved, and such products in total form a small percentage of a refinery's output—often grouped as 'other products' in their more summarized reporting. They need not be considered further in this chapter, which is concerned with how the refining industry meets the overall balancing requirements of main grade demand, and its fluctuation both now and in the future.

In this context, 'main grade products' will be expressed in simple terms as being the relative proportions required of gasoline, middle distillate (kerosines, jet fuel, gas, and diesel oils), and fuel oil to meet a market demand.

That such marketing demands have varied widely from region to region, and between countries in a given region, may be seen from the following tabulation:

Total oil products market demand in selected countries, 1981

(Percentages by volume)	Motor gasolines	Gas oil/ diesel fuel	Fuel oil	Others
United States	43	21	13	23
United Kingdom	31	26	22	21
West Germany	22	44	13	21
France	21	37	20	22
Italy	16	30	42	12
Japan	13	16	37*	34
Netherlands	11	23	30	36

* Includes crude for burning.

Source: Shell Briefing Service Booklet, Number 2, 1982, *Oil and Gas in 1981*.

Some of the above demand variations have been satisfied by international trading and the movements whereby a surplus make of a product, e.g. motor gasoline, is exported to balance deficit makes in other countries. (The UK has been a net importer of motor gasolines and a net exporter of gas oil.) However, it is not surprising that such diversities as in the above Table are not met by interchange alone, and that in a country like the US where fuel oil represents

only about 14 per cent by weight of total refinery demands and that for motor gasoline is high, the typical refinery is complex with downstream conversion units to maximize the production of motor gasoline. In contrast, in Western Europe and in Japan, where fuel oil has been about 35 per cent and almost 50 per cent by weight of total refinery make respectively, much less intensive refining patterns have sufficed with, until comparatively recently, often a number of refineries little more complex than the simple hydroskimming refinery as depicted in Fig. 2 of Chapter 10 on the Petroleum Refinery.

Since 1973, the share of oil in the energy use of the OECD countries overall has fallen from 54 per cent to 47 per cent, and total energy use in industry is declining. This decline in the share of oil is expected to continue, with 'oil substitution' a trend wherein in industrial use and power generation, for example, there is an increasing switch from the use of fuel oil to other energy forms such as coal, nuclear energy, and natural gas.

The pattern of petroleum product demand in the non-US countries of the OECD, such as Western Europe, is converging closer towards that of the US, with priorities towards making those products which cannot readily be replaced from other energy sources, such as transportation needs which will continue to be based on gasoline, jet, and diesel fuels for the foreseeable future.

THE CHANGE OF REFINING PATTERNS TO INCREASE GASOLINE AND MIDDLE DISTILLATE YIELDS AND REDUCE FUEL OIL

In countries such as the UK consumption of fuel oil has virtually halved since 1973, and it has been estimated that the share of fuel oil as part of the overall European product market will fall from the present 35 per cent possibly to 25 per cent by the year 2000 (*Petroleum Review*, May 1982).

In an earlier chapter of this book the difference in yields of the different light and heavy constituents of various crudes has been mentioned, and it is of interest to compare the difference in product patterns that may be obtained from, for instance, a typical medium-heavy Middle East crude of about 31–33° API gravity, and say a North Sea or similar light crude of about 40° API, when both are run in a simple hydroskimming-type refinery with no 'conversion processing':

Yields (volume)	Medium-heavy crude (%)	North Sea (%)
Gasoline	21	23
Middle distillate* (kerosine/gas oil)	33	39
Fuel oil	46	38

* There is some adjustment in the proportions between kerosine and gas oil, by adjusting distillation cut-points, and also between gasoline and middle distillate proportions (see later).

Some heavy and high-viscosity crudes will give even higher yields of fuel oil and less distillate products. It will be seen from the foregoing that although there can be some choice of yields by selecting the mix of crudes to be run, the

variation that will be obtainable is still somewhat limited by this means alone, particularly as the availability of light crudes is more restricted than that of heavier crudes. As in the US refining pattern therefore, the trend is to the increasing installation of conversion processes whereby the choice of either the thermal cracking, catalytic cracking, or hydrocracking route is taken to convert fuel oil components into lighter distillate products. Processes in each of these three categories have been installed or are being constructed in many of the former hydroskimming-type refineries.

Illustrative Yield Shifts

The types of yield pattern that may be obtained from the above routes are illustrated below:

Case 1 (the base case) is the hydroskimming refinery—a simple refinery without conversion, consisting of a crude distillation unit, a hydrodesulphurization unit for the middle distillate, and a catalytic reformer (Fig. 2, in Chapter 10 on the Petroleum Refinery). Case 2 is the case where mild conversion by a thermal cracker has been added. Cases 3 and 4 illustrate higher conversion, by the addition of a catalytic cracker (Case 3), and in Case 4 a hydrocracker with its associated hydrogen unit.

Yields from Different Process Schemes
(% by weight on crude oil)*

Product yield	Case 1 Hydro-skimming (base case)		Case 2 Hydro-skimming plus thermal cracking		Case 3 Hydro-skimming plus catalytic cracking		Case 4 Hydro-skimming plus hydro-cracking	
	A	B	A	B	A	B	A	B
Gasoline	15	20	20	24	22	35	26	40
Middle distillate	35	30	41	37	43	31	44	30
Fuel oil	46	46	33	33	28	27	21	20
Refinery fuel	4	4	6	6	7	7	9	10

* Yields on wt % no loss basis on crude.

Source: Chapter 10. 'Automotive Development from an Oil Company View.' K. R. Williams. *Proceedings of the Institute of Petroleum 1978 Annual Conference.* London. Heyden and Son.

The A and B sub-cases in the above Table correspond to a maximum middle distillate and maximum gasoline operation respectively, achieved by variation of the selected cut-points.

VISBREAKING

The visbreaking (or viscosity breaking) process is a mild form of thermal cracking, in which the conversion to material in the gasoline and gas-oil range is

kept low, but is used to reduce the viscosity of crude distillation straight-run residues (and sometimes also their pour point). It has the advantage in the case where a simple refinery operation is 'viscosity critical', i.e. where in the distillation of a heavy crude the viscosity of the residue fuel oil would be in excess of the saleable specification, and part of the straight-run gas-oil distillate yield would otherwise have to be blended back to meet the fuel oil viscosity limit. While new units may be constructed, in some cases a redundant surplus crude distillation plant may well be modified to perform the visbreaking function. A typical yield of a hydroskimming refinery plus simple visbreaker could lie intermediate between those of Cases 1 and 2 in the previous Table, e.g. say 39 per cent fuel oil yield.

COKING

Coking, as its name indicates, is the most extreme form of thermal cracking in which the ultimate of total extinction of fuel oil is practised, the heavy residue feedstock being pyrolysed to produce lighter boiling liquids which can be processed further into motor gasoline blend components and middle distillate, with a remaining yield of by-product coke which can be disposed of as solid fuel.

A yield case for a refinery with fluid coker could be 36 per cent gasoline, 42 per cent middle distillate, fuel oil nil, and coke 8 per cent—the ultimate in fuel oil reduction. In the two-stage flexicoking process, there is an added gasifier stage in which the coke product can be turned into a low BTU gas.

The coking process, of which there are a number of forms, is also usable for such feedstocks as bitumen, tar sands, and heavy non-conventional crudes that are non-fluid at ambient conditions (when the latter come into production).

CONCLUSION

With various combinations of the above conversion routes it is possible for refineries to adapt to a wide variety of crudes, and to a declining market for heavy fuels as oil substitution by coal and other energy resources paves the way for what in the future may ultimately be the all premium distillate product refining operation.

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Energy Conservation in the Oil Industry

By P. JONES

Its large internal fuel consumption and the large increase in costs of energy have resulted in the energy costs of a refinery now accounting for a quarter to nearly a half of total operating cost, compared to a figure of about 10 per cent in 1973. Thus the incentive for energy conservation within the oil industry itself is now great. This is achievable by thorough reappraisal of all heat and other energy uses against their current economics, for example by installing additional heat exchange in refinery process units that at former fuel cost would not have been an economic investment; by optimizing combustion efficiency by reducing excess air levels, for example by a change from natural-draught burners in process heaters, where excess air could be as high as 30 40 per cent, to more efficient forced-draught burners, which will also have more effective flame shape, together with stack heat recovery units installed to preheat feed, raise steam or preheat boiler feed water; by increasing the regularity and efficiency of onstream cleaning of heat-exchange surfaces (see Chapter 10 on Refining), and the use of anti-fouling inhibitors; the revising of the standards on the insulation of pipework, process vessels, and storage tanks, and where possible eliminating the intermediate cooling and reheating of intermediate products by feeding, e.g. hot residue, from one process unit direct to the next, so cutting out the intermediate tankage. Process conditions are also checked to ensure that excess reflux ratio above the degree of separation required in the distillation processes, or too high a column pressure, are not adding needlessly to heat input loads above that for the production specification.

Very considerable savings have thus been made within the industry, reported to be of the order of 20 per cent over the period 1972–1980 for one group of 33 refineries operated by a major oil company, and representing alone a saving of some 2.5 million tonnes of fuel per annum.[2]

The above improvement in energy use had a breakdown cited as follows:

40 per cent due to improved fuel consumption in process furnaces,
14 per cent due to lower steam consumption in process units,
10 per cent due to lower steam consumption in tank farms,
10 per cent due to lower steam supply to auxiliaries and buildings,
24 per cent due to lower hydrocarbon losses (treated here as part of the energy consumed).

It is significant that more than half of the improvements in efficiency were achieved by fine tuning of the units and increased maintenance, and less than half by capital spent on equipment changes. Further overall increases in energy efficiency are forecast from hundreds of small improvements envisaged to reduce energy use by a further 20 per cent over the next five years. In this a major impact will be in the operational sphere in optimizing process conditions, assisted by the use of microprocessors and computers as data

loggers. The inefficiency of older equipment can also be mitigated by selective replacement and by installing improved new equipment, i.e. by retro-fit; thus approaches should be aimed equally at older units, as at the design of new. The former case arises particularly for equipment used for generating heat and electricity. A useful approach to these analyses, where it is often possible to achieve *both* an energy cost saving *and* an accompanying saving in *capital cost* by attention to thermodynamic fundamentals, has been developed in a UK Institution of Chemical Engineers user guide *Process Integration for Efficient Use of Energy, 1982*;[3] the technique is applicable both to refining and chemical process plant.

A necessary caution when fuel consumption is reduced in a heater or boiler by a change to more efficient burners, or additional heat is extracted from combustion gases by installing added heat recovery exchange equipment, is that the flue gas volume and temperature will be lowered. This may cause the velocity up the stack to fall below that sufficient to maintain effective plume rise and dispersion of flue gas from the chimney. In such circumstances a solution can be to install an inner flue stack or liner in the chimney, to constrict flue diameter and restore stack velocity; an example is given in the UK Department of Energy monthly bulletin *Energy Management*, October 1982.

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Distillation

By R. PRIESTLEY, A. ARROWSMITH,
C. McDERMOTT and N. ASHTON

INTRODUCTION

Historical

SINCE the start of the petroleum industry the function of the refinery engineer has been to produce economically a marketable range of products from the complex mixture of hydrocarbons available in crude oil. In the earliest days of the industry when the main product of a refinery was lamp kerosine a distillation process was used to separate the desired components from the crude oil. As demand for kerosine increased it was soon apparent that the refiner was faced with the necessity of marketing that part of the crude oil which remained after the kerosine fraction had been removed. The refiner was able to meet this problem by further separation of the crude oil into a range of marketable fractions, and again a distillation process enabled him to do this.

After 1930 the demand for products in the lower boiling point range led to a relative surplus of higher boiling point products from the primary separation of crude oil components. The consequent development of thermal cracking processes enabled the refiner to match the yield of products with the pattern of market demand. At this stage in the development of refinery processes the principal products were fuels, lubricating oils and bitumen. In most cases the degree of separation required was not high, and distillation techniques already practised in other industries, for example alcohol rectification, were adequate with only slight modification.

With the dramatic increase in demand for high-octane aviation fuels and high purity feedstocks for petrochemicals during the war of 1939 45 the separation processes assumed a new importance. This trend has continued with the introduction of catalytic cracking and conversion processes and, while other separation processes are available and widely used, distillation is still predominant.

With the expansion of the petrochemical industry, there has been a shift in product demand. While the demand for gasoline and diesel fuels has continued to expand, the requirements of feedstocks for chemical processes have altered the product split from each barrel of crude.

The dramatic change in crude prices in the 1970s has led to increasing conservation of energy within the refinery. Traditionally distillation is wasteful in energy terms, since high grade heat is used in the reboiler and discarded as low grade heat in the condenser system. Methods of integrating heat loads throughout a chain of distillation columns are of growing importance. The use of pump-around systems to operate at nearer to minimum energy requirement is also increasing.

Separation Processes

The first decision that must be made by a refiner when presented with a separation problem is the choice between a chemical or a physical process. In general a physical method will be preferred but is not always feasible. For example, the separation of sulphur compounds will be achieved in most cases by hydrogenation, sulphuric acid treatment or caustic washing. Almost invariably, as in these examples, the products of the chemical reaction will be separated by some physical process.

The common methods of physical separation are:

Distillation is applicable to the separation of more and less volatile components in a mixture. The greater the difference in volatility between the components to be separated, the easier will be the separation.

Absorption the components of a mixture of gases may be separated by contacting the gases with a liquid solvent. The effectiveness of the process is dependent on the difference in solubility of the gases to be separated and the ease of recovering the dissolved component from the solvent.

Although usually classified as a physical separation method many absorption processes involve a chemical reaction between the solvent and the soluble component. In these cases it is preferable that the rate of reaction is high and easily reversible for the regeneration of the solvent.

Liquid–liquid extraction—is an attractive method of separation of components in the liquid phase where an immiscible solvent is available that selectively dissolves one (or a group) of the components in the mixture. In order to complete the separation it is necessary to recover the solvent from both the solvent-rich (extract) and solvent-weak (raffinate) phases in a subsequent separation stage.

Adsorption—the concentration of a component on the surface of a porous solid provides a method of separation that may be especially attractive when the concentration of the adsorbed component to be removed from the mixture is very low. The process is applicable to mixtures in either the liquid or the vapour phase. Regeneration of the solid adsorbent is effected either by heating or by steam stripping, most usually on a semi-continuous basis.

Less common processes—include fractional crystallization, thermal diffusion, reverse osmosis, ultrafiltration, batch and continuous chromatography, which are applied to rather special and infrequently encountered separation problems.

Classification of Distillation Processes

The common feature of all distillation processes is the tendency for the concentration of the more volatile component (mvc) in the vapour phase to be greater than that in the liquid phase when the two phases have been in contact.

In simple distillation the enrichment of the more volatile component is achieved by partially vaporizing a liquid mixture and allowing the two phases to separate. The liquid feed is vaporized either by raising the temperature or by reducing the pressure. A distillation column containing a number of separation stages arranged vertically is required to achieve a higher degree of separation (Fig. 1).

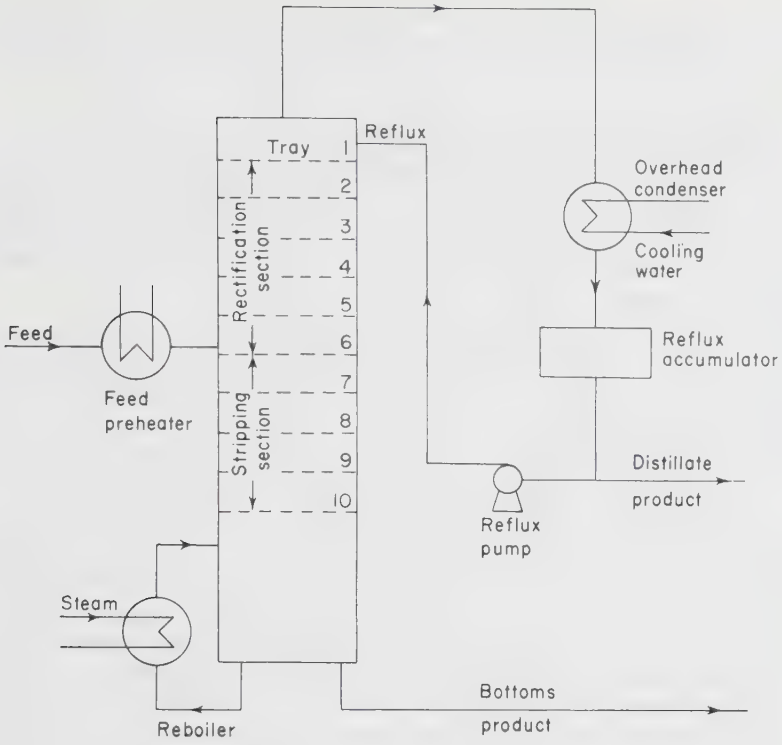


Fig. 1. Continuous stagewise distillation.

In stagewise operation the descending liquid passes through a number of stages where it is contacted by a countercurrent flow of ascending vapour. Below the point at which feed is introduced to the column (the stripping section) the more volatile component is stripped from the descending liquid. Above the feed point (the rectifying section) the concentration of the less volatile component in the vapour is reduced. In practice the stages are provided by plates designed to contact reservoirs of liquid with the ascending vapour.

In differential operation the countercurrent streams of liquid and vapour are contacted continuously on the surface of a packing material.

The distillation operation may be further classified in that simple, stagewise and differential distillation can be carried out batchwise or continuously.

Economic Significance

Few data are available on the capital expenditure on distillation equipment in the petroleum industry, but surveys show that the cost of distillation columns accounts for 10–12 per cent of the total investment in process equipment. The total cost of the equipment directly associated with the columns is of the order of three times that of the columns alone.

The distillation process also determines the capacity of the installations that provide steam, fuel and cooling water for the refinery.

Multiple Columns, Sequencing of Operations

With a multicomponent mixture $n - 1$ columns would be required to produce n pure products. It is important to select the correct sequence of distillation operations. The number of possible sequences rises very rapidly with the number of components (products) to be recovered. King (1971) has presented four heuristic sequence-selection methods; to quote:

1) Separations where the relative volatility of the key components is close to unity should be performed in the absence of non-key components.
2 Sequences which remove components one by one in column overheads should be favoured.
3 Sequences which give a more nearly equi-molal division of feed between the distillate and the bottoms should be favoured.
4) Separations involving high specified recovery fractions should be reserved until last in the sequence.

These basic rules are often conflicting, but do help to reduce the possible number of sequences.

Alternatively this process may be performed in one column with intermediate boiling point fractions withdrawn as side streams. This method is most attractive where a high degree of separation is not required and where the intermediate products are of a composition corresponding with the composition in the rectification section of the column (that is above the feed tray). The side stream is withdrawn from the column as liquid and the light ends are removed in a small ancillary stripper column.

A second comparatively rare need for taking a side-stream product arises when the accumulation of a component in a section of the column would interfere with separation of the key components.

DISTILLATION THEORY

Although distillation has been employed as a separation process for more than two thousand years the elements of distillation theory were not understood until the very end of the nineteenth century. Since then our understanding of the process has increased considerably, and ultimately we may be able to predict the performance of distillation equipment from a knowledge of the component properties. As present, however, the theory is incomplete and the empirical information required in practice is considerable.

Vapour Liquid Equilibrium

The study of most distillation problems must begin with an estimate of the distribution of the components between the liquid and vapour phases. The starting point most widely used has been Raoult's law which relates the partial

pressure of a component to its concentration in the liquid solution at equilibrium—

$$p_i = x_i P_i$$

where p_i = partial pressure of the component i
x_i = mole fraction of component i in solution
P_i = vapour pressure of pure component i at the same temperature.

From Dalton's law the partial pressure of a component and the total pressure of the system are related by,

$$p_i = y_i P$$

where y_i = mole fraction of component i in the vapour
P = the total pressure of the system.

Combining these laws we obtain

$$y_i / x_i = \frac{P_i}{P} = K_i$$

where K_i is constant at a specified pressure and temperature and is known as the 'phase equilibrium constant'.

Thus the distribution of a component between vapour and solution may be expressed as a function of temperature and pressure. The simple relationship is applicable to some ideal systems, including the straight-chain hydrocarbons containing 3 to 10 carbon atoms at temperatures not within 30 °C of the critical temperature of the system. 'K' values are available for such ideal systems in the form of charts and nomographs.

For the estimation of equilibrium ratios of non-ideal solutions the selection of the semi-empirical correlations applicable to the system will depend on the computing facilities available and the degree of accuracy required.

As a consequence of the ready availability of computers in recent years, there has been great progress in the field of phase equilibria correlation and prediction. In the petroleum industry methods are available for estimating 'K' values largely based on equations of state with empirically determined constants. Although crude oil is a complex mixture of many components, specific crude types may be characterized as 'pseudo-components' to enable computer programs to be used for distillation design. Many commercial organizations offer a complete service of equilibrium data prediction and column calculation.

Operating Pressure

The relative volatility of the key components to be separated increases with decreasing pressure and the ease of separation is favoured therefore by reducing the operating pressure of the fractionating column. However, the column capacity is in most cases controlled by the vapour capacity which is approximately proportional to the square root of the pressure. In practice the effect of pressure on column capacity is more significant than on ease of separation, and the most economic operating pressure is close to the maximum

at which the overhead vapour can be condensed with available cooling media. Where one or more of the components to be separated is heat sensitive, then the operating pressure corresponding with the maximum permissible temperature is selected. In this case the cost of maintaining a higher vacuum outweighs the benefit of increased relative volatility.

Steam distillation is a useful technique whereby a material which is immiscible in water may be distilled at a reduced temperature. By injecting live steam the partial pressure of the material to be distilled is maintained well below the total pressure in the column.

Equilibrium Flash Distillation

When a liquid mixture is partially vaporized and the vapour and liquid are allowed to separate there is an increase of concentration of the more volatile components in the vapour phase, and of the less volatile components in the liquid phase. The partial vaporization may be effected either by heating the liquid or by reducing the pressure. The degree of separation is not high but may be increased by carrying out the flash in a number of stages. Probably the most important application of this process is in the wellhead separation of dissolved gas from crude oil. By reducing the pressure from that at the wellhead in up to seven stages, with separation of the gas at each stage and recycle of flash liquid to each stage, the valuable C_4 and C_5 content of the crude can be increased, with a corresponding reduction of the lighter hydrocarbons.

Reflux Ratio and Number of Stages

In order to achieve a specified separation of two components both the reflux ratio and the number of stages may be varied over a wide range. The number of stages required is a minimum when all the condensed overhead vapour is returned to the column, *i.e.* 'total reflux'. The reflux ratio may be reduced to the point where the desired separation is achieved only with an infinite number of stages. Both the minimum number of stages (with total reflux) and the minimum reflux (with an infinite number of stages) are obviously impracticable conditions, but they are significant in prescribing the limits of these design variables and in indicating the ease of separation. An empirical correlation between functions of minimum and operating reflux ratios and the minimum and operating (number of) stages has been presented by Martin and Brown (1939) for hydrocarbon systems.

The choice of operating reflux ratio and the corresponding number of stages is an exercise in economic optimization. Increasing the reflux ratio decreases the number of stages and consequently the cost of the column, but increases the size of reboiler and condenser as well as the operating cost of the utilities. Quite frequently the optimum reflux ratio is rather less than 1.5 times the minimum, although with increasing energy costs the trend is towards operation at closer to minimum reflux. This leads to higher capital costs, yet allows savings to be made in running costs.

The relationship between the number of theoretical stages and the reflux ratio is shown in Fig. 2.

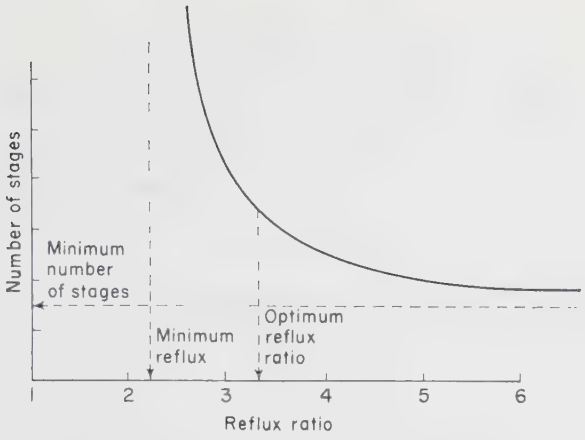


FIG 2. Relationship between the number of theoretical stages and reflux ratio.

Estimation of Number Stages

In continuous fractional distillation as practised in the petroleum industry the vapour/liquid contacting stages are provided in the form of plates. The vapour leaving a 'theoretical plate' or stage is in equilibrium with the liquid leaving that plate. Thus in a binary system

$$y_n = Kx_n \tag{1}$$

where y_n = mole fraction of more volatile component in vapour leaving nth tray
x_n = mole fraction of more volatile component in liquid leaving nth tray
K = equilibrium constant of more volatile component at the tray temperature and pressure.

The analysis of multistage fractionation is simplified very considerably if constant molal flow of liquid (L) and of vapour (V) may be assumed throughout a section of the column. In most hydrocarbon systems this assumption is valid because the molal latent heats are approximately constant and the heat of mixing is negligible. The tray to tray analysis without this assumption is complicated by the varying internal reflux ratios which must be estimated by enthalpy balances across each tray.

Assuming constant molal flows Sorel's mass balance equation for the section becomes

$$y_{n+1} = \frac{L}{L+D} x_n + \frac{D}{L+D} x_D \tag{2}$$

where D = moles of distillate product
x_D = mole fraction of more volatile component in distillate,

which with the equilibrium equation (1) provides a stepwise solution along the section.

A graphical solution based on these equations was proposed by McCabe and Thiele and has been widely applied to systems that are or can be considered as binaries.

TABLE I
Short Cut Methods

Variable	Author	Reference
Minimum number of stages	Fenske, M. R.	*Ind. Eng. Chem.*, 1932, **24**, 482
	Underwood, A. J. V.	Trans. Instn Chem. Engrs, 1932, **10**, 112
Minimum reflux ratio	Colburn, A. P.	*Trans. A.I.Ch.E.*, 1941, **37**, 805
	Underwood, A. J. V.	*Chem. Engng Prog.*, 1948, **44**, 603
Number of stages/reflux ratio for hydrocarbons organics	Martin, H. Z. and Brown, G. G.	*Trans. A.I.Ch.E.*, 1939, **35**, 679
	Gilliland, R. E.	*Ind. Engng Chem.*, 1940, **32**, 1101
Feed plate location	Kirkbride, C. G.	*Petrol. Refining*, 1944, **23**, 32
Distribution of key components	Geddes, R. L.	*A.I.Ch.E.J.*, 1958, **4**, 389

Short-cut methods continue to be of interest for both preliminary estimating and development studies. The short-cut methods listed in Table I allow the estimation of the number of theoretical stages at a selected reflux ratio. It is not to be expected that the accuracy of these empirical methods is very high.

Rigorous solution of the material and energy balance and equilibrium equations for multicomponent distillation has now become a routine matter using a digital computer. The organization of the calculation has moved from the tray to tray methods of the early days to exploit the many sophisticated methods for the solution of systems of equations, linear and non-linear, currently available. Whatever the method chosen, it is usually necessary to impose a 'convergence' method such as the 'theta' method of Holland (1983) to force the closure of the overall material balance. The choice of method in a particular case is related to the number and boiling range of the components, non-ideality of the system and whether energy balances are required, etc. Many commercial organizations now offer computer packages in which a number of alternative methods are tried automatically until a solution is reached.

The availability of such calculation methods makes parametric investigations of column design variables fairly straightforward, thus facilitating the production of an optimal column design.

Holland (1983) has recently reviewed the column calculation methods available, including the theta method, Newton–Raphson and methods for highly non-ideal systems. Distillation with chemical reaction and systems of interlinked columns are also included, together with methods for unsteady-state calculations.

Continuous Contact (Differential) Distillation

In differential distillation processes (Fig. 3) the vapour and liquid are brought into contact countercurrently and continuously throughout the column, which produces a continuous concentration gradient for each component in both the vapour and liquid phases. The concentration driving force promoting the mass

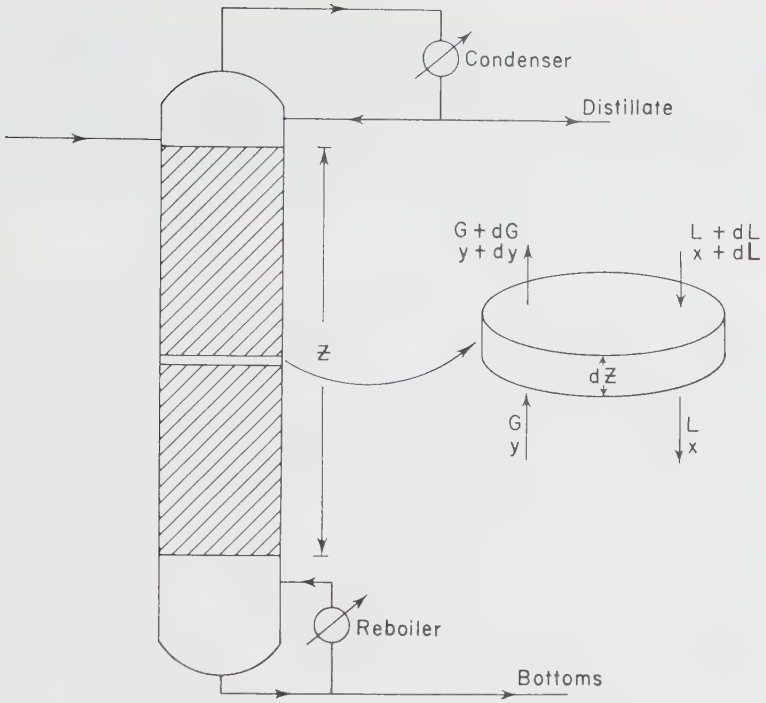


FIG. 3. Differential distillation.

transfer of the more volatile component across the vapour/liquid interface will be $y - y^*$ where

y = mole fraction of mvc in vapour
x = mole fraction of mvc in liquid
y^* = mole fraction of mvc in a vapour in equilibrium with a liquid containing an mvc concentration of x.

From a material balance over an increment of the column cross-section and integrating it may be shown that the height of column, Z, required to produce a change of concentration from y_1 to y_2 is

$$Z = \frac{G}{K_y a} \int_{y_1}^{y_2} \frac{dy}{y - y^*}$$

where G = moles of vapour flow/unit cross-section
K_y = overall mass transfer coefficient (overall gas)
a = interfacial area per unit volume.

The assumption implicit in this relationship is that G, K_y, and a remain constant throughout the column.

The function

$$\int_{y_1}^{y_2} \frac{dy}{y - y^*}$$

measures the difficulty of the separation and defines the 'number of transfer units' (NTU) required for the duty. The height of a transfer unit (HTU) is a measure of the efficiency of the contacting device and is equal to $Z/(\text{NTU})$.

With multicomponent mixtures it is more common to use the theoretical plate approach to determine the required number of stages and to consider the packing efficiency in terms of the 'height equivalent to a theoretical plate' (HETP) in order to obtain the height of packing required.

DISTILLATION EQUIPMENT

The countercurrent contacting of liquid and vapour involved in the fractionation process is normally carried out in vertical cylindrical columns. In equilibrium stage devices vapour is bubbled through the liquid retained on a vertical array of plates or trays. The extent to which the vapour leaving the tray approaches equilibrium with the liquid from the tray is a measure of the tray efficiency. In an alternative arrangement—differential fractionation—the vapour and liquid are contacted continuously. Most usually the differential column consists of one or more sections of packing material. The function of this packing material is to provide a large vapour/liquid interface as the descending liquid is brought into contact with the ascending vapour.

The choice between use of a tray column or a packed column is based on economic considerations. Generally a tray column will require the smallest capital investment, but new developments in packing design are leading to specialist packings being the preferred choice. Also, scale of operation affects the economic decision. In small columns, less than 3 ft in diameter, packings often provide the optimum design. Again, pressure of operation can lead to the use of packings even in very large diameter columns, for example in vacuum distillation where the inherent pressure drop across a tray would be unacceptably high.

Equilibrium Stage Trays

The selection and design of equilibrium stage plates should take into account the wide range of conditions that are encountered in refinery operations. Among the criteria that should be given consideration are—

(1) The efficiency of vapour/liquid contacting in so far as the tray efficiency determines the number of actual plates required for a specified separation.
(2) The capacity of the tray, as it determines the diameter of the column for the design load.
(3) The flexibility of the tray and its ability to accommodate varying vapour and liquid loads.
(4) Robustness of construction.
(5) The effect of corrosion, suspended solids, and gum and polymer formation on tray performance.

Tray Efficiency

The 'Theoretical Tray' was defined as a tray on which the exit streams of vapour and liquid attain thermodynamic equilibrium. In practice, equilibrium is not achieved and an 'Actual Tray' will provide less separation than a theoretical tray. Thus, an overall tray efficiency, E, may be defined as

$$E = \frac{N_{\text{Theoretical}}}{N_{\text{Actual}}} \qquad (N \text{ is the number of plates})$$

for the required separation.

Tray efficiency is a complex function of system physical properties, tray design and operating variables, and cannot be predicted reliably. The design engineer relies largely on experience and experimental data from existing columns.

In the absence of any practical data, the method of O'Connell (1946) probably gives the most reliable estimate. This relates overall efficiency to the molal liquid viscosity of the feed at the operating conditions and the feed volatility.

Effectiveness of vapour/liquid contact

The mass transfer between the liquid and vapour phases is determined by both the physical properties of the system and the geometry of the tray. The effects of both are interrelated.

The physical properties which affect the efficiency significantly are—vapour and liquid densities; vapour and liquid diffusivities; vapour and liquid viscosities; surface tension and relative volatility.

In hydrocarbon systems it is generally supposed that the liquid viscosity is the property that may be most closely correlated with the tray efficiency.

The geometrical factors which appear to be most important in their effect on the effectiveness of the vapour/liquid contacting are weir height, 'F' factor, and length of liquid path. The weir height controls the liquid hold-up and the residence time of the vapour in contact with the liquid. In most hydrocarbon systems extending the immersion of the slots or perforations beyond $1\frac{1}{2}$ inch does not appreciably increase the efficiency.

The 'F' factor is defined as $V\sqrt{\rho}$ where—

V = the superficial vapour velocity
ρ = vapour density.

In general as 'F' is increased the efficiency increases to a maximum and then decreases rapidly as entrainment of liquid droplets from the liquid on the tray becomes the controlling factor, as illustrated in Fig. 8.

In larger diameter columns the length of the liquid path across the tray has an important effect. It is entirely possible in these larger columns to achieve tray efficiencies appreciably greater than 100 per cent. However, while increasing the liquid path length increases the effectiveness, because of the cross-flow effect, the hydraulic gradient generated by the liquid flow will in some circumstances result in unacceptable mal-distribution of vapour and dumping of liquid through the tray.

Recent research has attempted to quantify the effect of liquid back-mixing on large trays. Its effect is to reduce the tray efficiency owing to a reduction of the composition gradient along the flow path length. In single-pass large diameter trays, stagnant zones may be present at the shell between the weirs. Multi-pass trays (Fig. 5) have many advantages in large diameters, for example the stagnant zones are eliminated, and the hydraulic gradient is reduced. In general, the liquid path length should not exceed 5 ft and multiple passes are used to keep within this criterion.

Entrainment

The effectiveness of a tray will be reduced if either liquid from one stage is transferred to the tray above, or vapour is transferred to the tray below, i.e. if there is either liquid-in-vapour entrainment upwards in the column or vapour-in-liquid entrainment down the column. The most important effect is to reduce the concentration gradient in the column. A secondary effect is to increase the gross liquid and vapour loads in the column.

Liquid-in-vapour entrainment is a function of vapour velocity, liquid and vapour densities, tray spacing and surface tension. An entrainment rate of up to 4 per cent is acceptable in most columns, although column diameters based upon the widely quoted Souders–Brown equation yield lower entrainment rates above atmospheric pressure.

Vapour-in-liquid entrainment is controlled by providing adequate residence time in the downcomer of the tray. For most hydrocarbon non-foaming systems a residence time of 10 s reduces the entrainment to an acceptable level. This suggested residence time may have to be doubled for foaming systems or in columns where a high temperature gradient exists.

Tray Capacity

The ultimate loading of a tray is usually determined by the condition of 'flooding'. This is when the liquid height in the downcomer becomes equal to the tray spacing and there is no longer sufficient hydraulic head for the liquid flow to overcome the tray pressure drop.

A general operating envelope is shown in Fig. 4.

Flexibility of Operation

In the selection of a suitable tray for refinery distillation some consideration should be given to the fluctuation of vapour and liquid loadings that may arise in operation. The required operating range of loadings may be influenced by possible changes in feed rate and composition as well as by the product specifications.

A simple tray will suffice for those applications where a turndown ratio of 2:1 is adequate for the range of operating conditions that are encountered in perhaps half the columns in a refinery. With more elaborate tray designs it is claimed that turndown ratios of 9:1 are possible.

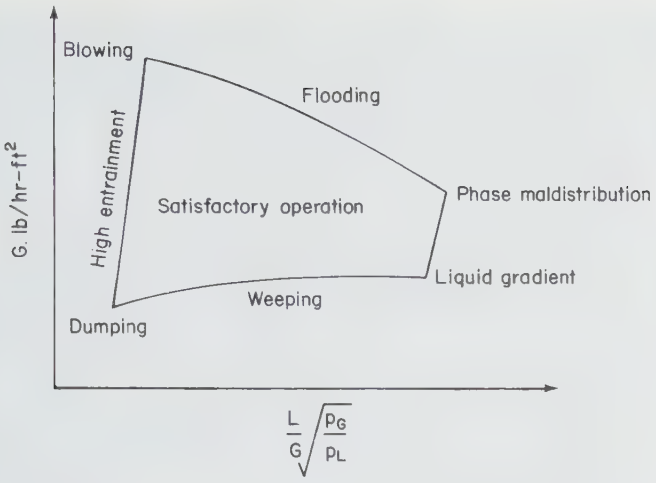


Fig. 4. Effects of vapour and liquid loadings on sieve-tray performance (Fair, 1963, p. 556. Reproduced with permission from B. D. Smith, *Design of Equilibrium Stage Processes*. © 1963 McGraw-Hill Book Company).

Mechanical Construction

In most refinery conditions it is economically attractive to provide trays of considerable robustness that can guarantee trouble-free operation over long periods of continuous operation. Loss of production due to corrosion or mechanical failure has become increasingly costly with increase in plant capacity. Mild steel trays are fabricated in 10–12 gauge sheet material and alloy trays in 14–16 gauge material in more severe corrosion conditions.

Usual practice is to install the trays supported on angle rings welded on to the column shell. The trays themselves are assembled with removable sections with provision for access for cleaning and maintenance. Tray spacing is also controlled by access considerations and is commonly greater than would be economic if entrainment alone were the criterion.

Tray Designs

The number of tray designs that have been developed and are in use in refinery distillation columns is now very great, but may be classified into four main groups—bubble-cap trays, perforated trays, valve trays, and trays without downcomers.

Bubble-cap trays

Bubble-cap trays were the most popular type of tray to be installed in refineries until 1964, and are still to be found operating in the majority of columns in the older established refineries throughout the world. In terms of reliability and flexibility these trays are not unsatisfactory, but are now installed only rarely because of their comparatively high initial cost.

The tray consists of a segmental plate supported round its periphery by the column wall, and downcomers delivering liquid from the tray above to the tray

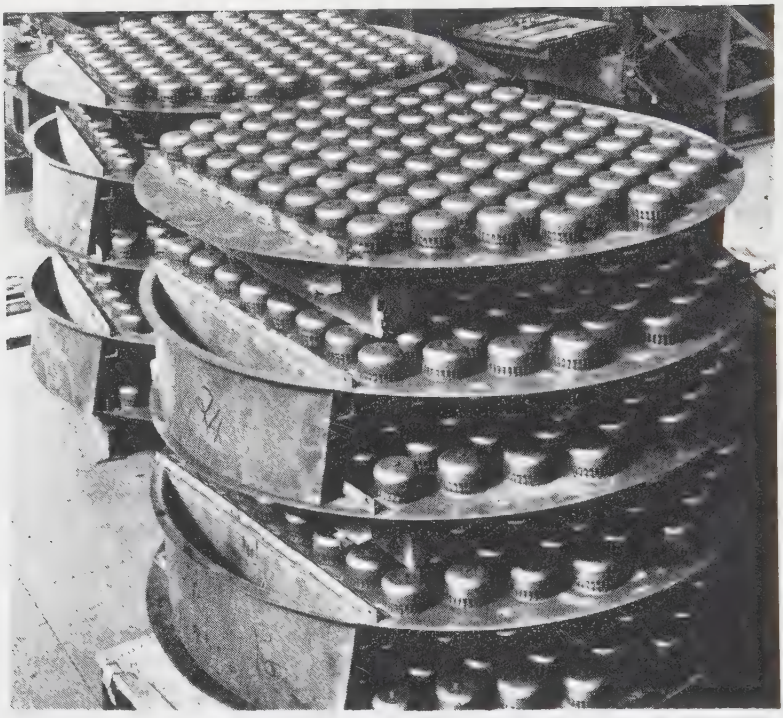


Fig. 5. Bubble-cap trays before installation (courtesy Metal Propellers/APV).

below are provided at each end. An outlet weir plate controls the liquid hold-up on the tray. Between the downcomer sections caps are held in position over orifices fitted with risers. Typically the capped area of the tray is 75 per cent of the superficial area of the column and the riser area 10 per cent of the capped area (Fig. 5).

Vapour rising from below the plate flows through the risers, is reversed by the cap and is introduced into the liquid on the tray through slots provided in the vertical skirt section of the cap. Caps are usually circular $1\frac{1}{2}$–6 inch diameter, but may be rectangular or polygonal. The slots are frequently trapezoidal or rectangular, but may be triangular or in rare cases not present at all.

At very low vapour loadings contacting efficiency is low with pulsating flow through the slots and at high vapour loadings entrainment is high. The liquid load is limited by downspout capacity, which when exceeded causes flooding of the column, or an excessive hydraulic gradient across the tray. The consequence of this gradient is mal-distribution of vapour through the tray. In extreme cases vapour ceases to flow through the caps adjacent to the inlet weir and liquid back-traps to the tray below. The hydraulic gradient may be reduced by a factor of eight by arranging the tray for double-pass flow.

The advantages of the bubble cap tray are claimed to be—

(1) Reasonably high efficiency (60–90 per cent with light hydrocarbon systems)

(2) Stable operation over a wide range of loads (turndown ratio 4:1)
(3) No moving parts (not susceptible to small quantities of solids or polymer formation)
(4) May be designed for large liquid hold-up—which varies only slightly with change of load.

The main disadvantages are—

(1) High initial cost
(2) Relatively high pressure drop
(3) Large hydraulic gradient at higher liquid loadings.

Perforated Trays (or sieve trays)

Although perforated trays were used in distillation columns before bubble-cap trays and were popular in the air separation field, it is only recently that this type of tray has gained general acceptance in the oil industry. Because of its simplicity and consequent cheapness the perforated tray has almost completely superseded the bubble-cap tray in those refinery services where the higher flexibility of the bubble cap is not essential.

The arrangement (Figs 6 and 7) is similar to the bubble-cap tray, with circular perforations of usually $\frac{1}{8}$–$\frac{1}{2}$ inch diameter in the bubbling area arranged on triangular or square pitch so as to provide a free (hole) area of between 8 and 14 per cent. The smaller hole diameter generally yields a slightly superior performance but at greater cost. An increase in free area results in a lower pressure drop and higher capacity but reduces the operating range of the tray.

The peak efficiency of a well designed perforated tray is at least as high as that of a bubble-cap tray for most hydrocarbon systems. Because entrainment is less at higher vapour loadings, rather smaller column diameters may be designed. Alternatively, the capacity of a bubble-cap column may be increased appreciably by replacing the bubble caps with perforated trays. In a number of cases it has been possible in this way to increase the throughput of refinery installations by as much as 100 per cent. In comparison with a bubble-cap tray the perforated tray has the advantage also of a very low hydraulic gradient at normal liquid loadings.

The most significant disadvantage of the perforated tray is the reduction of tray efficiency at low vapour loadings. Because there is no positive liquid seal on the tray there is a minimum vapour velocity below which liquid is 'dumped' through the perforations to the tray below. The loading at this 'weep point' is a complex function of the tray geometry and the physical properties of the system but the controlling variables appear to be the vapour velocity through the perforations, the gas density and the head of the liquid on the tray. As a first approximation the vapour loading at the 'weep point' is equivalent to an atmospheric air velocity through the perforations of 40 ft/s with the usual 1–1$\frac{1}{2}$ inch w.g. of liquid hold-up on the tray.

Some characteristics of sieve trays are given in Table II and their efficiencies in Fig. 8.

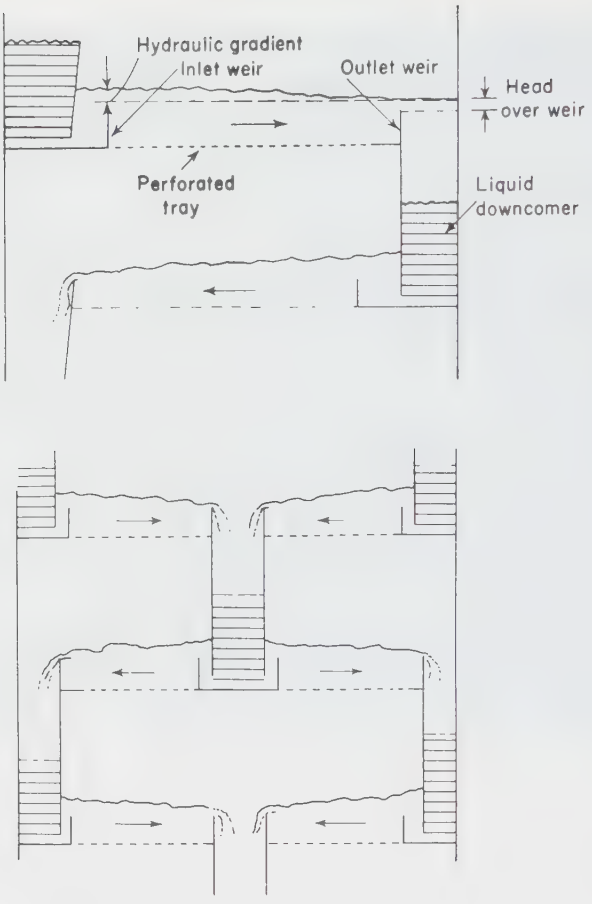


FIG. 6. Perforated tray. Single pass (above), split flow (below).

Valve trays

The valve tray has been developed to meet the demand for a distillation tray which is capable of operating efficiently over a wider range of loadings than can be accommodated by a perforated tray and yet is considerably cheaper than a bubble-cap tray.

The common feature of the many proprietary designs available is an orifice area on the tray which increases automatically as the vapour load in the column increases. By use of this device it is feasible to operate at a high efficiency with a vapour loading down to one ninth of the maximum loading. In addition it is claimed that in comparison with bubble-cap trays these trays have the desirable characteristics of low pressure drop, low hydraulic gradient, low entrainment, and high scouring action on solids tending to settle on the tray deck.

The orifice in the tray deck is often about $1\frac{1}{2}$ inch diameter but may be rectangular. In one design of valve the edge of the orifice is formed to provide a

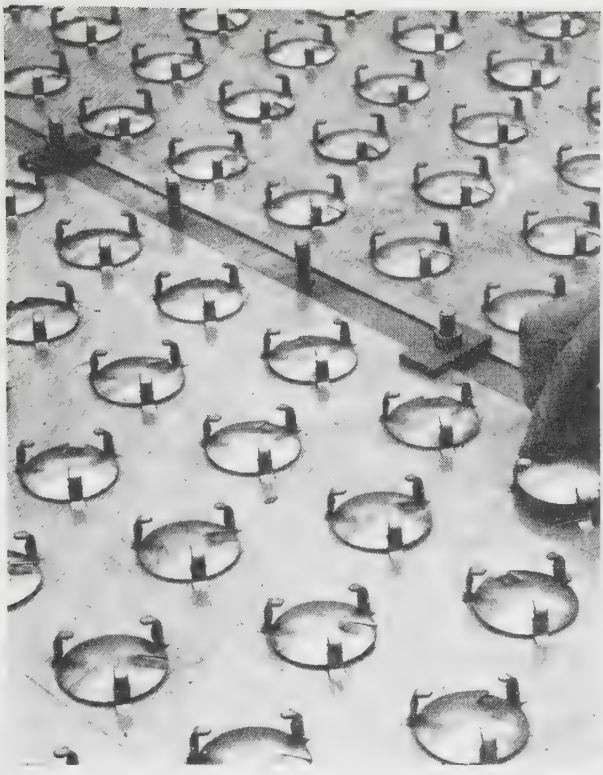


FIG. 7. Part of McKeown valve tray (courtesy Mass Transfer Ltd).

TABLE II
Some Characteristics of Sieve and Valve Trays

	Sieve			*Valve*			*McKeown Valve*	
	Plastic	Mild steel	Stainless steel AISI 304	Plastic	Mild steel	Stainless steel AISI 304	Mild steel	Stainless steel AISI 304
Costs	1.0	1.0	4.0	1.2	1.2	4.5	1.2	4.4
Installation costs	0.8	1.0	1.0	0.85	1.05	1.05	1.0	1.03
Flexibility	3 to 1	3 to 1	3 to 1	8 to 1	6 to 1	6 to 1	8 to 1	8 to 1
ΔP	1.05	1.0	0.95	1.15	1.1	1.05	1.1	1.05
Capacity	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Wear	Good	Excellent	Excellent	Average	Good	Good	Excellent	Excellent

N.B. (1) The datum cost is based on mild steel sieve trays with 12.5 mm holes, 10 swg deck thickness, 10% hole area, 10% downflow area, and 3 m diameter single-pass.

Courtesy: Mass Transfer Ltd.

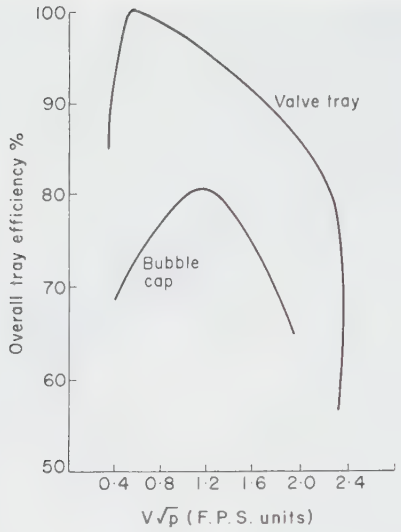


Fig. 8. Tray efficiency of bubble-cap and valve trays.

'venturi' shaped opening with a consequent reduction in pressure drop. The moving part of the valve is a domed disc fitted with 'legs' which locate the disc in position over the orifice and control the valve lift. As the vapour load in the column is increased the number of valves in the open position increases. Although the hydraulic gradient on the tray is small it is sufficient to ensure that the rows of valves adjacent to the outlet weir open first as the load is increased.

Because of the moving parts in the tray the operation of the tray is adversely affected by gums and polymers. The other disadvantages arise from the relatively fragile construction of the valve which are liable to damage during installation and maintenance. The erosive conditions in the orifice area may also lead to tray failure.

Among the most recent developments in valve-tray design may be mentioned the so-called 'fixed valve' tray where the domed disc and 'legs' are formed by a pressing from the tray deck, and a British design where the 'legs' are integral with the tray deck.

Some characteristics of valve trays are given in Table II and their efficiencies in Fig. 8.

Packed Columns

Equilibrium stage devices are strongly favoured by the refinery engineer, but in exceptional circumstances differential distillation may provide the best means of separating components of differing volatility. A packed tower may be preferred when the column diameter is less than 3 ft, a very low pressure drop per theoretical plate is desirable, or construction in ceramic, glass or plastic materials is necessary because of the corrosive nature of the system.

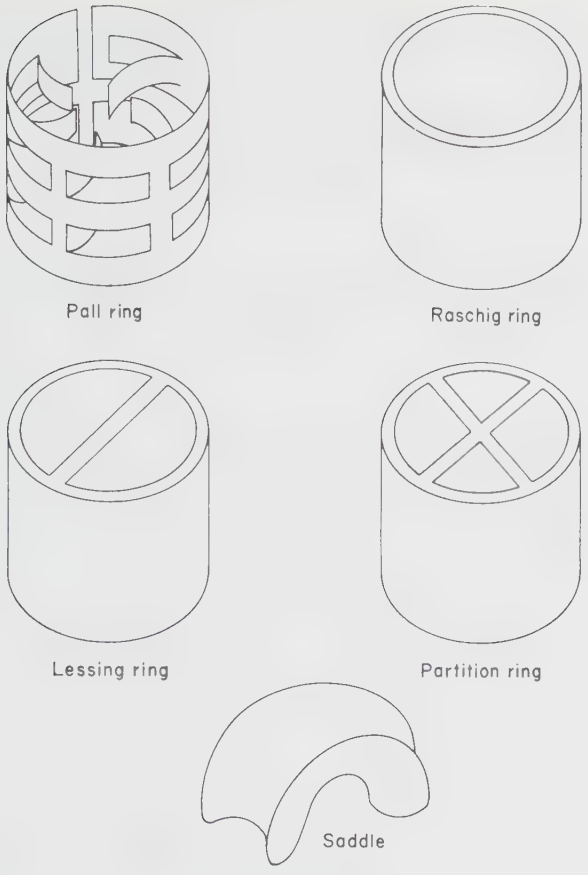


FIG. 9. Random packings.

A very wide range of packing materials is available of which the most popular in refinery practice include—

(a) Ring packings (Fig. 9) are normally dumped (or random) packed. The Raschig ring is the simplest and has been the most popular, but because of superior capacity/contacting effectiveness—pressure drop characteristics the Pall ring is very often economic. Ring packings are available in the range $\frac{1}{2}$ to $3\frac{1}{2}$-inch diameter in metal, ceramic and plastic materials.

(b) Saddle packings (Fig. 9), of which the Berl and Intalox are the best established forms, provide a random packed bed with a larger surface area and low pressure drop. Saddles with one or more orifices have been developed, and these are claimed to improve performance further.

(c) Regular packings have gained more general use in recent years, because of their improved flow characteristics and resulting high

capacity and low pressure drop. Specialist packings for vacuum distillation are available, e.g. Sulzer, Knitmesh, Glitsch Grid.

(d) New designs of random packing are claimed to be replacing trays in large refinery towers. An example is the Metal Intalox packing (Norton Chemical Process Products).

Packing Performance

The factors which affect the performance of a packing and which are relevant in the selection of the most economic packing, apart from the initial cost, include the liquid and vapour capacity, vapour/liquid contacting efficiency, pressure drop (Fig. 10), liquid hold-up, resistance to corrosion and mechanical strength.

The pressure drop/boil-up rate characteristics of random packings of the type used in distillation are a function of the packing but follow a common pattern. The line representing log (pressure drop) versus log (boil-up rate) has two discontinuities. With increasing boil-up rate the first discontinuity coincides with a rapid increase in liquid hold-up which defines the 'load point'. The second discontinuity occurs when the column floods and defines the 'flood point' and the maximum capacity of the column.

The vapour/liquid contacting efficiency of typical random packings increases rapidly at low boil-up rates until the liquid flow rate is sufficient to wet the surface of the packing. Above this 'minimum wetting rate' the contacting efficiency increases slightly to reach a maximum between the 'loading' and 'flood' points.

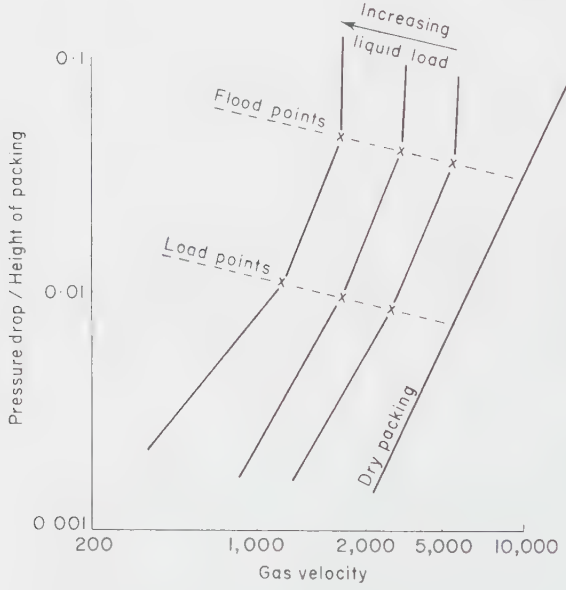


Fig. 10. Pressure drop characteristics of random packing.

For random packings the capacity is a function of a/ε^3.

where a = surface area of packing
ε = fractional voidage in bed

and the physical properties of the system. In general a/ε^3 decreases with the size of packing element and the largest packing element compatible with satisfactory vapour/liquid distribution is found in most cases to be the most economic.

With the new generation of packings, the group a/ε^3 has been found to be inadequate for the correlation of capacity. Empirically determined packing factors have now taken its place and values are available from manufacturers.

Packing Efficiency

In general, the mass transfer efficiency of a packing is even more difficult to predict than that of a tray. Again, as with trays, efficiency is dependent on packing type and material of construction, system physical properties and operating conditions.

The efficiency is expressed as the Height Equivalent to a Theoretical Plate (HETP) and must be determined experimentally, preferably by taking data from large industrial towers.

ANCILLARY EQUIPMENT

The cost of the distillation columns is only a small part of the capital investment involved in the installation of a distillation process. For the typical refinery plant the columns will amount to some 10–15 per cent of the total cost of the equipment. Of comparable, if not greater, cost will be the heat exchangers, piping and instrumentation. Additionally, the cost of accumulators, pumps, steel structures and foundations together exceeds the cost of the fractionating columns.

Heat Exchangers

The range of duties for the heat exchangers in a distillation process includes—feedstock preheating and vaporization, condensation or partial condensation of the overhead vapour, reboiling of column bottoms, and cooling of liquid products before discharge to a further processing unit or storage.

The *tube-in-shell* type of heat exchanger, because of its compactness and ease of maintenance, has proved most popular in refinery service. High rates of sensible heat transfer are promoted by high fluid velocities and by arranging a pattern of countercurrent flow between the tube and shell side fluids. These factors are controlled by the number of 'passes' as determined by the arrangement and spacing of baffles. The three forms of tube-in-shell construction encountered are—

(a) *Fixed tube sheet units*—are fabricated with tube sheets welded integral with the shell. This is the least expensive tubular exchanger, and is selected for those duties where mechanical cleaning of the outside of the

tubes is not required and where the temperature difference between the tubes and shell is not sufficient to cause excessive thermal stresses in the tubes. By incorporating an expansion bellows or a glanded joint in the shell it is possible to accommodate the differential thermal expansion—most readily in the shells of smaller diameter.

(b) *Floating head type units*—are some 25 per cent more expensive than the fixed tube sheet construction. The floating head being free to move, stresses due to thermal expansion are eliminated, and because the bundle can be withdrawn from the shell, the outside of the tubes is accessible for mechanical cleaning.

(c) *Hairpin type tube bundles*—are rather less expensive than floating head units. Like the fixed tube sheet unit they have the advantage of no internal joints that might lead to contamination of one stream by the other. The bundle is withdrawable for cleaning and the tubes are not subject to thermal stresses. However, the inner surface of the hairpin tubes cannot be cleaned mechanically, so that this type of unit is limited to those applications where the tube side fluid is relatively clean.

Water-cooled condensers are of a similar tube-in-shell construction, arranged with the vapour condensing on the outside of the tubes and cooling water on the more readily cleanable inside of the tubes.

During the last decade the replacement of water-cooled heat exchangers and condensers by air-cooled units (Fig. 11) has become increasingly attractive. Fresh water supplies for cooling purposes have become more scarce and expensive, while sea water cooling involves either heavy maintenance costs or the use of expensive corrosion-resistant materials of construction. Extensive

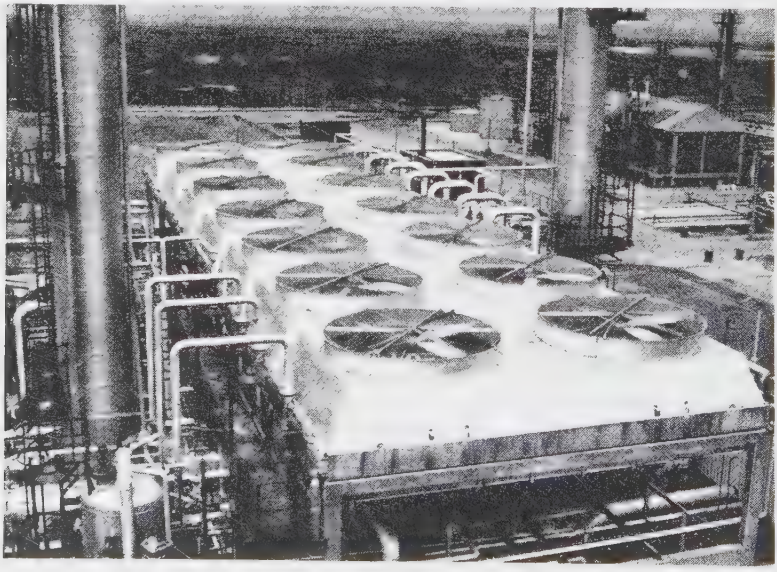


FIG. 11. Air-cooled heat exchangers in a UK refinery (courtesy of G.K.N. Ltd).

economic studies of the problem have demonstrated that although the air-cooled exchangers may be more expensive in first cost, they are often more economical because of the lower operating charges.

The typical air-cooled exchanger consists of 4 to 6 row deep rectangular banks of extended surface tubes with axial flow fans providing a flow of air across the outside of the tubes. For temperatures up to 150°C the extended surface tubing is most usually round steel tubing with aluminium spirally wound fins, although elliptical tubes with rectangular fins appear to be gaining acceptance because of the lower power consumption associated with the lower air side pressure drop. Depending on the number and height of the fins the tube area can be reduced by a factor of up to 20 when compared with unfinned tube area. The greatest benefits from the use of air-cooled units are gained when the fluid to be cooled is at a relatively high temperature and provides a high heat-transfer coefficient inside the tubes. The application of air cooling is limited by the approach of the outlet temperature to the dry bulb ambient temperature so that the minimum temperature attainable may be some 5–10°C higher than with cooling water. A further disadvantage of air-cooled units is that the space requirement is considerably in excess of that required for the equivalent water-cooled unit.

Less common types of heat exchanger used in the refinery include—

Tube-in-tube heat exchangers, which consist of an array of coaxial tubes or pipes, are used for low heat-load duties. They are especially useful for handling viscous fluids when the inner tube is preferably of the extended surface type.

Scraped surface heat exchangers may be effective where solids, e.g. waxes, precipitate on cooling. The heat transfer surface is maintained clean by rotating blades.

Submerged coil cooling units are frequently employed for the cooling of high temperature viscous residues. The coil carrying the hot residue is immersed in water to which heat is transferred by natural convection.

Direct contact condensers, in which the vapour to be condensed is brought into direct contact with water sprays. These condensers are suitable for handling hydrocarbon vapours from a distillation column operating under vacuum when the drum containing the vapour is fitted with a barometric leg to facilitate the removal of the cooling water.

Plate heat exchangers are increasingly popular in continental Europe where considerable development has produced designs suitable for process heat transfer duties. The very high heat-transfer coefficients obtainable in the fluids flowing between profiled plates yield a compact heat exchanger that is easily dismantled and cleaned. Earlier designs were limited in application because of the low pressure rating, but units designed for pressures of up to 250 p.s.i. are now available in a range of materials of construction.

The thermal energy for the fractionation process is supplied by partial vaporization of the liquid leaving the bottom tray of the column. In columns up to 1 ft in diameter sufficient heat for their purpose can be transferred through the surface of a steam-heated coil submerged in the liquid accumulated in the base of the column. For larger columns it is more convenient to perform this vaporization in a heat exchanger, known as a reboiler, located outside the distillation column.

A kettle type reboiler consists of a pool boiling section, a stripped liquid

accumulator and a liquid droplet disentrainment zone. The multitubular heating element is of the horizontal hairpin type for steam-heated reboilers, but may be fitted with a floating head if the heating medium is likely to scale the inside of the tubes. From the pool boiling section, the boiling liquid flows over the segmental baffle to the accumulator from which it is either removed as bottoms product or returned to the base of the column. The vapour space above the boiling liquid is designed to give a vapour velocity that will permit the disengagement of liquid droplets.

Thermosyphon type reboilers may be arranged either vertically or horizontally. In the more popular vertical arrangement liquid from the base of the fractionating column passes through the inside of the tubes of a fixed tube sheet shell and tube unit. The vapour/liquid mixture is returned to the column where an impingement plate is provided for separation of the liquid and vapour. The liquid level in the column, which controls the recirculation rate, is adjusted to ensure that the liquid/vapour ratio at the outlet is not less than about 3:1. In horizontal thermosyphon reboilers vaporization takes place on the outside of the tubes and the lower pressure drop (and elevation of the boiling point) increases the rate of transfer of sensible heat in the non-boiling section of the reboiler.

The advantages claimed for thermosyphon reboilers are—high heat-transfer rates by forced convection, low fouling of the heat-transfer surface because of the higher fluid velocities, and low capital cost.

Fired Tubular Heaters

The development of the pipestill and the replacement of shell stills made possible the high throughputs of today's crude oil distillation units. The feedstock passes through an array of tubes arranged in a refractory-lined shell that may be cylindrical or box shaped. The combustion of fuel oil or gas in burners located in the wall of the heater provides the heat which is transferred by both radiation and convection to the fluid inside the tubes (Fig. 12).

The type of heater selected will be determined by the heat load and the specified thermal efficiency and pressure drop of the heated fluid. Although vertical cylindrical heaters have been designed for heat absorption rates up to 150 million Btu per hour, this type of heater is usually favoured for much smaller heat loads. The advantages claimed for this construction include—

(1) Overall thermal efficiencies up to 65 per cent for the radiant section of the heater and up to 80 per cent when combined with a convection section in the stack.
(2) High uniformity of heat flux in the radiant section because of the symmetrical arrangement of floor burners with respect to the wall tubes.
(3) Maintenance of refractory walls is minimal because of protection from overheating provided by the tubes, and a shape resistant to the effect of minor explosions.
(4) Simple foundations and minimum ground space.

Box furnaces are preferred for the larger heat loads which are required, for example, in crude distillation units. The economic advantage arises from the

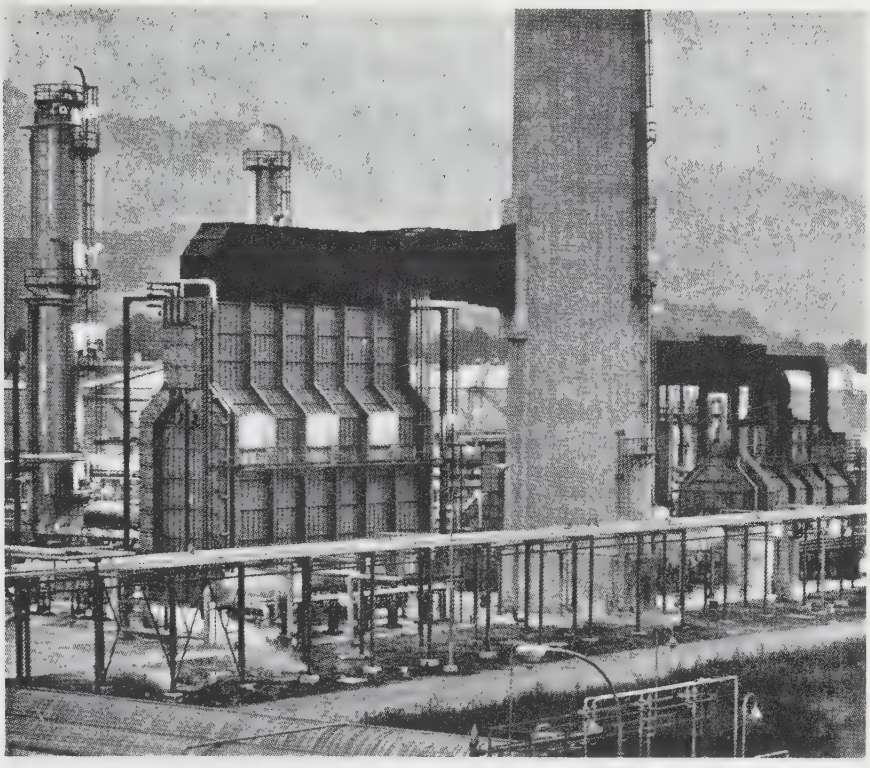


FIG. 12. Crude oil distillation unit heaters in a French refinery (courtesy G.K.N. Ltd).

greater length of tube that can be built into both the radiant and convection sections of the heater with a corresponding saving in the cost of return bends. A secondary advantage is the benefit of shop prefabrication with site assembly of the sections.

Especially in the larger heaters, the radiant heat transfer area, and consequently the cost, is influenced most by the permissible heat flux. With increasing heat flux the thermal efficiency declines, the 'film' temperature of the fluid inside the tubes rises with possible decomposition of the fluid and deposition of coke, and reduced tube life. For various heater duties maximum average permissible heat fluxes are specified in the range of 10 000–15 000 Btu per hour per square foot of tube area with the intention of limiting the maximum temperature of the fluid. Important factors which affect this maximum temperature at the specified average heat flux are—

(1) The degree of turbulence of the fluid in the tube. A low velocity of the fluid will result in high radial temperature gradients and therefore a high temperature at the fluid close to the surface of the tube. In practice the maximum turbulence will be provided that is consistent with the maximum acceptable pressure drop.

This factor has considerable bearing on the design of feed vaporizers in the vacuum distillation units of a refinery. The problem is particularly acute in this case because of the large increase in volume

that occurs as vaporization proceeds and the severe pressure drop limitation.

(2) Uniformity of heat flux along the tube length. The designer of the heater will have attempted to obtain as uniform a heat flux as possible, but some sections may still receive higher fluxes than others. Two major causes of mal-distribution are 'cold' or 'hot' areas caused by unsatisfactory flow of the hot gases and asymmetrical disposal of the tubes and refractory surface. A secondary cause of variation in the heat flux is frequently the change in the internal heat transfer coefficient along the tube length. Thus, in a distillation unit heater, the internal fluid to which the heat is transferred may be transformed in stages from a liquid receiving sensible heat, via a boiling liquid, to a vapour carrying liquid.

(3) Circumferential uniformity of heat flux. Hottel has demonstrated the effect on the distribution of heat flux of the tube arrangement with respect to the refractory surface and the radiating body of gas. He showed that the ratio of maximum to minimum heat flux may be reduced by, say, 50 per cent when instead of arranging tubes along the refractory wall they are located in the body of radiating gas. Heater designs which incorporate this feature have gained acceptance, especially where control of maximum temperature was critical.

(4) The tubes in the convection section exposed to the radiant section. The row of tubes at the inlet to the convection section receive the radiant heat flux from the radiant section together with a high convection rate from the gas flow into the convection section. In order to minimize the effect of this combined radiant and convective heat flux the tubes are cooled by the lowest temperature liquid feed available.

The convection section of a heater serves to increase the thermal efficiency by removing further heat from the flue gases leaving the radiant section. Typically the heat absorption in the convection section is 25–33 per cent of the radiant section load. However, more recent furnace designs aim to increase this percentage. With the exception of the 'shock tubes' in the inlet section the convection tubes are often finned. The merit of extended surface tubes in this application arises from an increased heat recovery rate with minimum pressure drop and a reduction in the weight which is often supported above the radiant section. With a 'dirty' fuel oil giving an appreciable ash, finned tubes would be unacceptable. In these circumstances either studded or (more probably) plain tubes would be used with provision for soot blowing.

An excess quantity of air supplied to the furnace can influence adversely the thermal efficiency in three ways. The temperature of the combustion space is reduced, the emissivity of the hot gases which is a function of the partial pressures of the water vapour and carbon dioxide is reduced, and the heat content of the gases to the stack is increased. Well designed and maintained gas or oil burners will operate with an air supply some 10–25 per cent in excess of that theoretically required for complete combustion. Inward leakage of air through the walls is controlled by balancing the burner and stack draughts so that the pressure of the gases entering the convection section is only very slightly below atmospheric pressure.

CONTROL OF DISTILLATION COLUMNS

The automatic control of distillation is well established in modern refinery operation using both pneumatic and computer-based systems. Increasingly, the controllers themselves are being replaced by microprocessors or process control minicomputers. These are then likely to form part of a distributed system allowing centralized control of the complete plant. For reasons of safety, the final control elements will usually be pneumatically activated, and all such components whether pneumatic or electrical should be protected to the appropriate I.P. Standard. The requirements of the distillation control system however implemented are, of course, efficient and economic operation consistent with safety and stability. The large energy demands of the distillation columns within the refinery mean that if control is directed towards minimizing such demands, the savings produced can be significant. Shinskey (1979) has pointed out that, because the distillation process is difficult to control and sensitive to upset, operators tend to over-purify as a matter of course. Such a policy is expensive as far as energy is concerned, and a well designed control system should allow operation closer to product specification.

The control scheme chosen in a particular case will depend more on the separation and characteristics of the column involved than on the hardware of the control used. In what follows, the representation will be in terms of pneumatic systems for purposes of clarity. However, for some of the more complex schemes, for example, involving some kind of dynamic model of the process, suitable pneumatic devices would not be available and the implementation would be by means of a computer.

The column control schemes to be discussed involve the allocation of usually five manipulated variables, namely, distillate, bottoms, reflux and coolant flows, and boil-up rate to the maintenance of pressure, product compositions and reflux drum and reboiler levels.

Control of Pressure

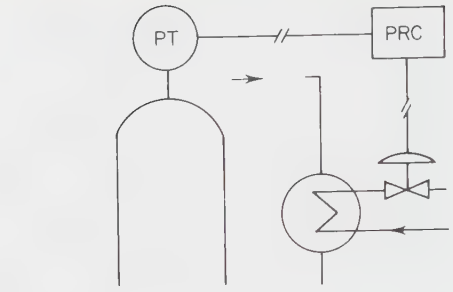
As will be seen later, product flows, boil-up and reflux flow, although affecting column pressure, are usually chosen for material balance and quality control. The heat transferred in the condenser is a common means of closing the energy balance.

A cheap form of pressure control is produced by manipulating the flow of cooling water from the condenser as shown in Fig. 13(a). This is satisfactory provided that the response is sufficiently rapid. A residence time of the water in the condenser not exceeding 45 seconds is desirable. It is, of course, necessary to allow for the least favourable conditions, for example minimum cooling water temperature and heat load with clean condenser tubes.

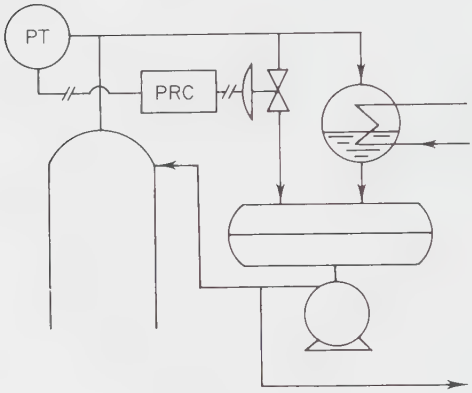
The alternative use of an air-cooled condenser is often more satisfactory, but the equipment required to regulate the flow of air is likely to be expensive.

More rapid response in the case of a total condenser may be obtained using the arrangement shown in Fig. 13(b). Here a hot vapour by-pass to the accumulator is used to limit the pressure drop available to the condenser, thus raising column pressure when the by-pass valve is opened.

The size of the by-pass control valve depends on the pressure drop available.



(a)



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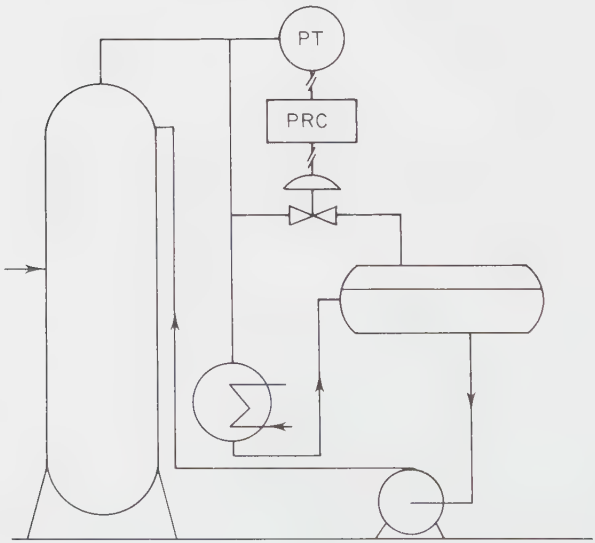

(c)

FIG. 13. Control of pressure by (a) Coolant flow, (b) Vapour by-passs, (c) Vapour by-pass with submerged condenser.

With the condenser located beneath the accumulator, as shown in Fig. 13(c), the pressure drop is increased allowing the use of a smaller valve. The further advantage of this method is that with the condenser at ground level, steel work costs are reduced and there is good access to the condenser for cleaning and maintenance.

When operating at atmospheric pressure, a vent from the condenser will usually provide sufficient regulation, air being drawn into the system to limit the rate of condensation when the pressure falls and expelled otherwise.

The control of pressure in vacuum distillation can be achieved by manipulating a bleed of air or inert gas to the vacuum pump, but the possible build-up of inerts can lead to operating problems. The provision of a vent valve for the release of incondensible gases would therefore be necessary. The alternative of controlling pressure by the manipulation of a valve in the line to the vacuum pump is preferred.

Quality Control

The factors which influence product compositions in a distillation column may be most readily understood by examining the material balance equations for the column. Assuming constant separation, Shinskey has solved the resulting equations to determine the effect of varying the flow rate on the distillate and bottoms compositions. The form of the relationship is shown in Fig. 14, from which we see that manipulation of distillate flow rate has a significant effect on both product compositions. A similar plot may also be produced for bottoms flow with the result that either product flow can be manipulated to control a particular product composition. The product flow chosen for manipulation will usually be the smaller, whichever product is to be controlled.

The constancy of the separation means that, if one product composition is maintained, the other will also be held on specification. It would therefore appear to be sufficient to control only one product composition. Separation,

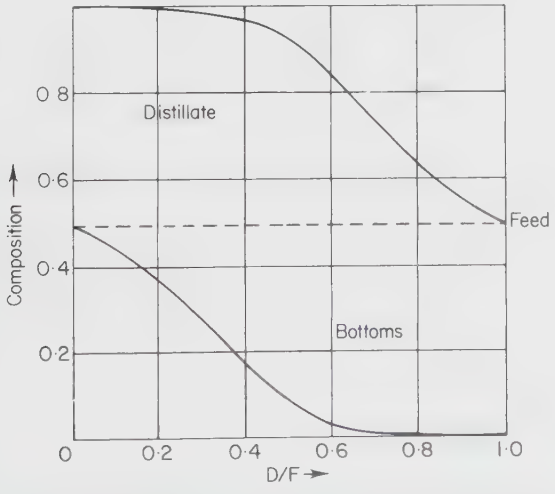

Fig. 14. Effect of distillate to feed ratio on product compositions.

however, depends upon the internal vapour and liquid flows in the column and it is necessary to take steps to preserve separation, usually by manipulation of boil-up or reflux flow rate.

The composition loop in distillation control is usually slow due to the physical form of the column which consists effectively of a series of stages each producing its own delay. The internal flows in the column must all readjust before a disturbance is fully corrected. It is evident then that composition detection should introduce as small a lag into the control loop as possible. Temperature is often used to infer composition and, provided composition is reliably indicated, the response time is correspondingly reduced. Temperatures of the product streams themselves are not usually used for control purposes, since the composition dependence of temperature is low at high purity. An investigation of the temperature profile in the column using one of the many steady-state simulation methods currently available will usually identify a point in the column, a few trays from the end, at which the temperature is a satisfactory indication of product purity.

Variation in the ambient pressure can introduce error into the conversion of temperature to an equivalent composition, and a widely used method avoiding this difficulty is the differential vapour pressure cell. This is a bulb containing a sample of liquid of the composition required on the tray under control which is placed in the liquid on that tray. The difference between the pressure on the tray and that exerted by the bulb is the error signal transmitted to the controller which then acts to reduce the error to zero.

Material Balance Control

When one of the product flows is used to control composition, the other flow must be used to preserve the material balance. This would be accomplished by using the second product flow to maintain level. For example, if distillate flow is to be manipulated to preserve its composition, bottoms flow would be used for reboiler level control. This then allows the choice of either:

(a) Using reflux flow to preserve accumulator level and leaving steam flow to the reboiler on set point control.
(b) Using reboil steam to maintain accumulator level with reflux flow on set point.

The second alternative (b) is likely to be more satisfactory in most cases because all column variables respond more readily to changes in boil-up rate.

A substantial part of the delay in the scheme as above is a consequence of the time constant of the accumulator. The level in the accumulator has to change before the reflux flow is adjusted. The situation can be improved by modifying the reflux flow to compensate immediately for changes in the distillate rate. This introduction of feed forward compensation considerably improves the response time of the loop.

Feed Forward Control

The solution of the material balance equations, which was used earlier to predict the effect of product flow rates on their compositions, can also be used to

predict the changes in product flows required to compensate for disturbances in feed composition and flow rate. As feed changes are the main load disturbances on the column and feedback control takes considerable time to correct for these, it makes good sense to instrument the feed for flow and composition, and correct for changes which occur in a feed forward mode. The essential requirement is to maintain one of the product flows as a linear function of the total flow of a key component in the feed. Similarly, corrections are made to the variable controlling separation, i.e. boil-up or reflux flow rate, so that ideally no change will occur in the product compositions. Usually, of course, only partial correction will be achieved, so that some feedback trim will be needed to restore the required operating conditions completely.

It is necessary, when designing the feed forward control system, to take account of the time taken for corrective action to produce its effect on the output. This may be in advance of, or lagging behind the effect produced by the disturbance. The corrective action then needs to be subject to a suitable lag or lead/lag element to ensure that the column outputs are corrected at the right time. Details of the types of dynamic compensation required for different combinations of load and manipulated variables are given by Shinskey (1979).

DISTILLATION PROCESS

Crude Oil Distillation

The primary separation of crude oil fractions in the most simple refinery is performed by continuous distillation at atmospheric pressure. Table III shows the yields and properties of the principal straight-run products from a typical Middle East crude.

Single-stage and three-stage crude oil distillation units are illustrated in Figs 15 and 16.

The crude oil distillation (or 'topping') operation differs from normal distillation practice previously described in that—

(a) The greater part of the heat of vaporization is supplied to the feed stream rather than by way of reboiling the liquid in the base of the column;
(b) Products of a volatility intermediate between the overhead and bottoms products are withdrawn as sidestreams;
(c) Live steam is injected into the base of the column and the side-stream strippers for the secondary control of the initial boiling point of the fractions.

Of all the units in a refinery the primary distillation unit is required to have the greatest flexibility in terms of variable quality of feedstock and range of product yields.

The maximum permissible temperature of the feedstock in the vaporizing furnace is the factor limiting the range of products in a single-stage (atmospheric) column. Thermal decomposition or 'cracking' of the hydrocarbons begins as the temperature of the oil approaches 360°C. This thermal decomposition is undesirable because the carbon produced tends to be deposited on the tubes, with consequent formation of hot spots and eventual

TABLE III
Yields and Properties of Straight-run Products from Middle East Crude

	Non-condensed gas	Gasoline	Kerosine	Gas oil	Fuel residue
Yield, % wt	1	15	12	17	55
B.P. range, °C	—	to 150	150–230	230–340	340
Specific gravity, 15/15°C	—	0.7	0.78	0.85	0.97
Sulphur, % wt	—	0.02	0.2	1.4	3.9

failure of the affected tubes. In the processing of lubricating oil stocks an equally important consideration in the avoidance of these high temperatures is the deleterious effect on the lubricating properties.

Vacuum Distillation

For the production of heavy gas oil, lubricating oil and bitumen fractions the reduced crude oil from the atmospheric column is further heated and vaporized in a direct-fired heater and charged to a vacuum column. Typically the flash

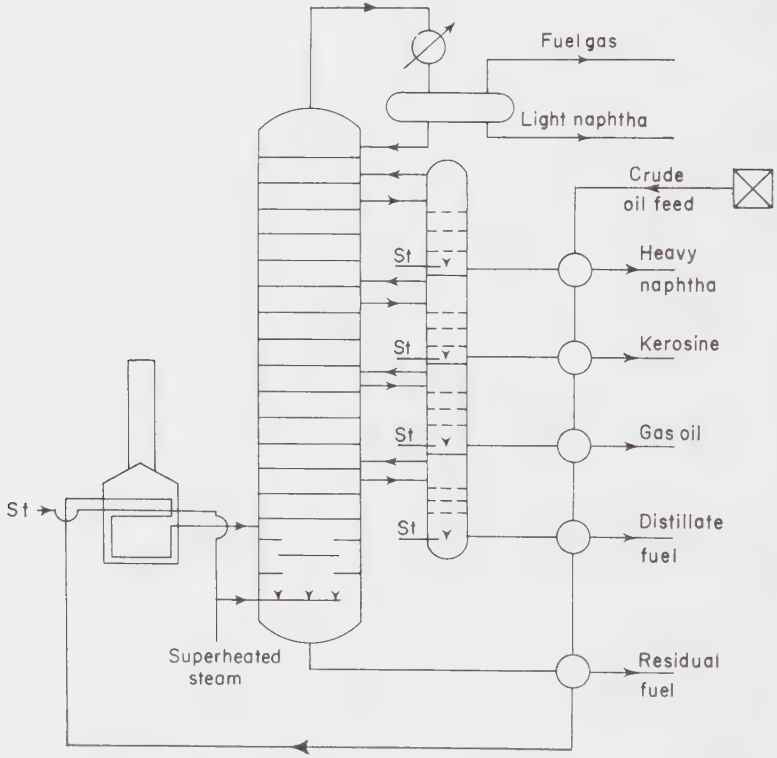

Fig. 15. Single-stage crude oil distillation unit.

temperature will be 390–400°C at 120 mmHg absolute pressure. The partial pressure of the hydrocarbons is effectively reduced still further by the injection of live steam. The steam added to the column, principally for the stripping of bitumen in the base of the column, may amount to 15 lb per brl of feed, and is superheated in the convection section of the heater.

When trays similar to those used in the atmospheric column are used in vacuum distillation the column diameter may be extremely large—up to 45 ft. In order to maintain low pressure drops across the trays the liquid seal must be minimal. Because of this low hold-up and the relatively high viscosity of the liquid the tray efficiency tends to be much lower than in the atmospheric column. For these reasons it would appear that trays in vacuum columns are being superseded by grid packings of proprietary design.

The vacuum is maintained in the column by removing the non-condensible gas that enters the column by way of the feed to the column or by leakage of air. Either mechanical pumps or multistage steam ejectors may be used, although the latter are usually most economical when used in conjunction with a barometric (direct contact) condenser.

Pre-treatment of Crude Oil

Crude oil that is contaminated with salt water either from the well or in transportation to the refinery must be treated to remove the emulsion. Both electrostatic and chemical methods are available. If salt water is not removed the materials of construction of the heater tubes and column intervals are exposed to chloride ion attack and the corrosive action of hydrogen chloride

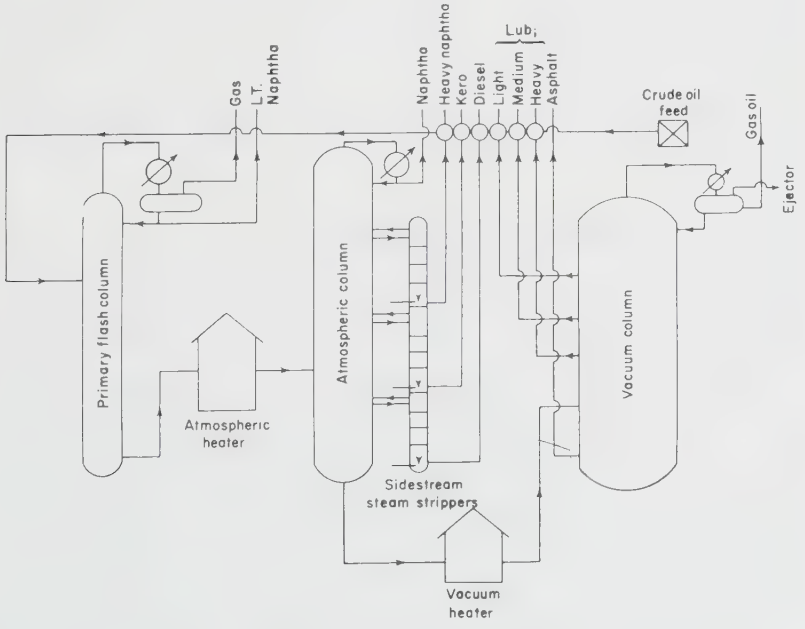

FIG. 16. Three-stage crude oil distillation unit.

which may be formed at the temperature of the column feed. Corrosion in the principal distillation column can frequently be reduced by preflashing the crude oil feed. The temperature of the feed is raised by heat exchange with the products from the distillation stages and fed to a preflash tower at a pressure around 2 3 atmospheres. Dissolved hydrogen sulphide may thus be removed prior to the atmospheric column which would otherwise be exposed to the corrosive attack of hydrogen sulphide at an elevated temperature and in the presence of steam.

The economics of crude distillation can frequently be improved by blending two, three or even more crudes, The optimization of feed composition with the pattern of market demand and plant capacity has received considerable attention in recent years.

Gas Separation

The increasing value of the light hydrocarbon fractions produced by the various cracking and reforming operations has led to the development of stabilization and gas recovery processes (Fig. 17).

In a typical system the mixture of light hydrocarbon gases and gasolines is fed at appropriate points into a stripper/absorber. The lower section of this column is reboiled to strip the methane and ethane from the heavier hydrocarbons which have been absorbed in the upper section of the column. The feed gases leaving the top of the absorber are desulphurized before passing to the refinery feed gas system.

The rich liquor from the absorber is in turn debutanized and depropanized by distillation, and the resulting gasoline is fractionated to produce light and heavy gasolines in a gasoline splitting column. A proportion of the heavy gasoline from this spitter is cooled and recycled to the top of the stripper/absorber as lean absorption oil.

By reducing the temperature and increasing the pressure of the stripper/absorber the system may be extended to recover the ethane–ethylene content of the gas feed.

Extractive and Azeotropic Distillation

In cases where two components of similar volatility are to be separated, the distillation process may be uneconomic because of the large number of stages required. The process may not be possible at all if the two components form an azeotrope.

The separation of these components of similar volatility may become economic if an 'entrainer' can be found that effectively changes the relative volatility. It is also desirable that the 'entrainer' is reasonably cheap, stable, non-toxic and readily recoverable from the components. In practice it is probably this last named criterion which limits severely the application of extractive and azeotropic distillation. The majority of successful processes, in fact, are those where the entrainer and one of the components separate into two liquid phases on cooling if direct recovery by distillation is not feasible.

A further restriction in the selection of an azeotropic 'entrainer' is that the boiling point of the entrainer should be in the range 10–40°C below that of the

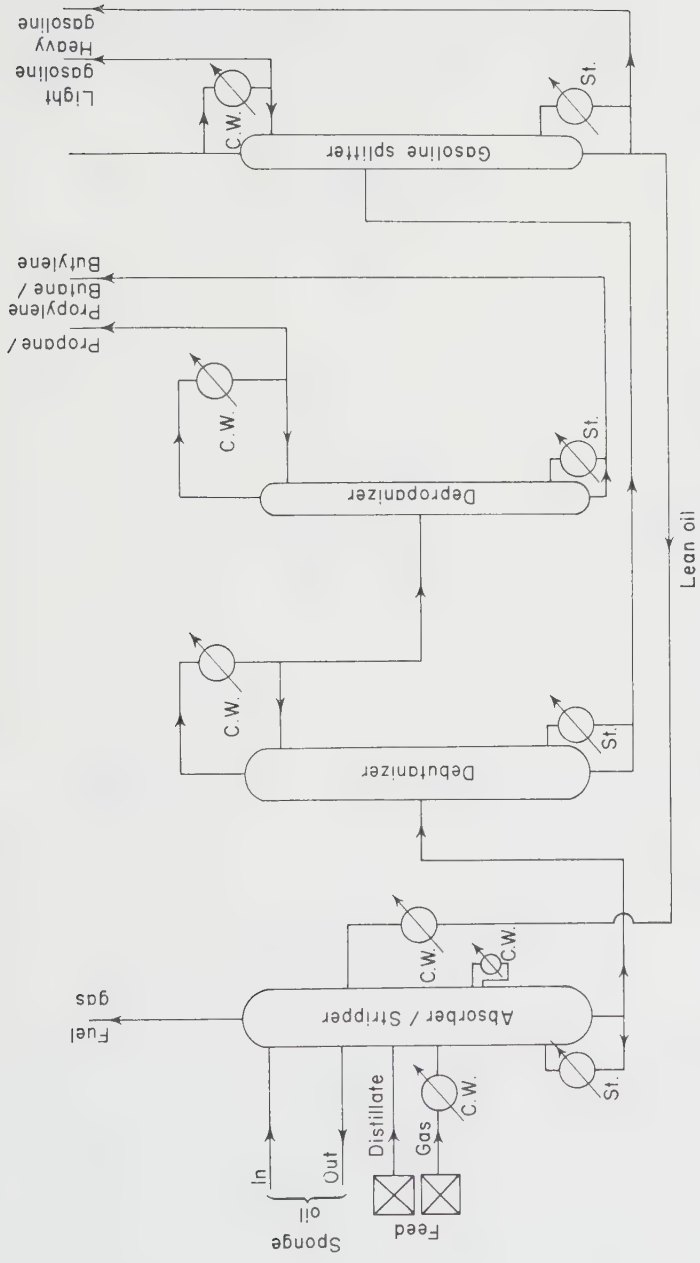

FIG. 17. Gas separation plant.

components. Thus while the 'entrainer' is more volatile than the components and distils off in the overhead product it is present in a sufficiently high concentration in the rectification section of the column.

The similarities and differences between azeotropic and extractive distillation may be illustrated by two processes that have been proposed for the separation of C_4 hydrocarbons (Figs 18 and 19).

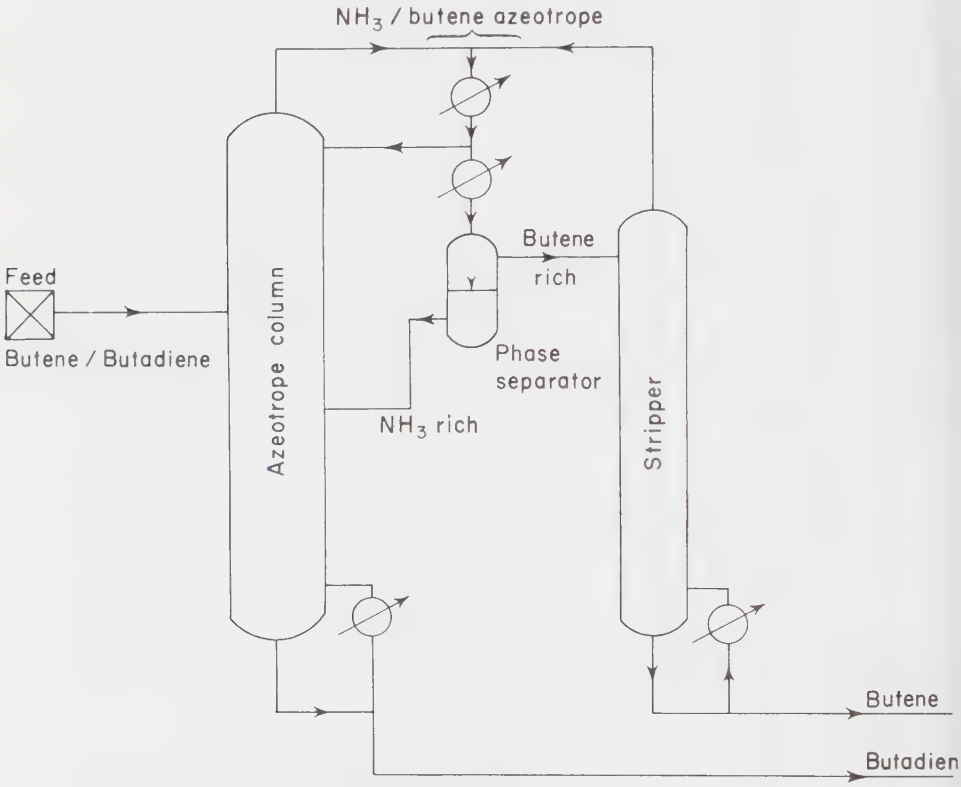

FIG. 18. Azeotropic separation of butene and butadiene.

Butadiene and butene may be separated by the use of liquid ammonia which forms an azeotrope with butene. The ammonia-butene azeotrope overhead from the azeotropic distillation is condensed, cooled and allowed to separate into a butene layer and a heavier ammonia layer. The butene layer is fed to a second column where the ammonia is removed as a butene-ammonia azeotrope and the remaining butene is recovered as bottom product. The ammonia layer is returned to the lower section of the first azeotropic distillation column. Butadiene is recovered as bottom product from this column.

Using acetone/water as an extractive solvent for butanes and butenes the butane is removed as overhead from the extractive distillation column with acetone/water charged at a point close to the top of the column. The bottoms

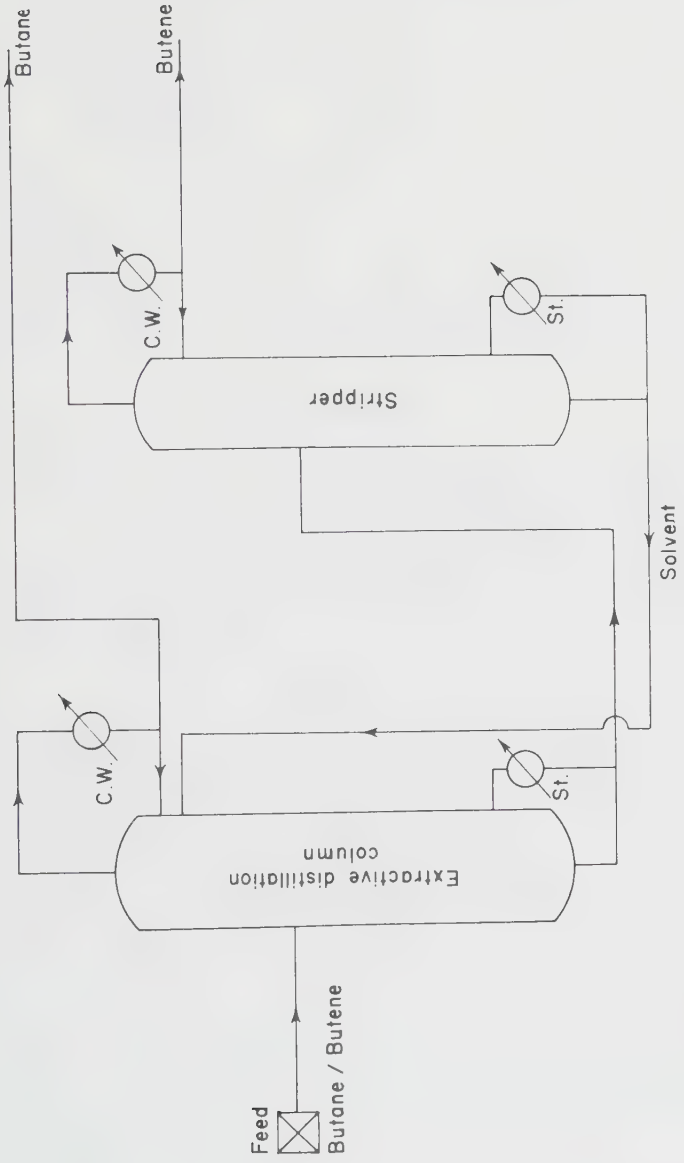

FIG. 19. Extractive distillation of butane and butene with acetone/water solvent.

TABLE IV
Azeotropic and Extractive Distillation Processes

Azeotropic distillation		Extractive distillation	
System	Entrainer	System	Solvent
Ethyl alcohol/water	benzene	Butadiene/butane	furfural
	trichloroethylene	Isoprene/pentane	acetone
2,5-Dimethylhexane/toluene	methanol	Toluene/paraffins	phenol
Butanes/butenes	ammonia	HCl/water	sulphuric acid

product of butenes and the extractive solvent is fed to a second column where the butenes are removed as overhead. The acetone/water solvent from the base of this column is recycled to the first column.

Some examples of azeotropic and extractive distillation processes of commercial interest are tabulated in Table IV.

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14

Cracking and Reforming

By L. J. McPHERSON and M. F. OLIVE

THERMAL CRACKING

Introduction

Thermal cracking can be described as the decomposition or 'cracking' of a hydrocarbon at elevated temperature to form material of lower molecular weight. Without a doubt this is the oldest hydrocarbon conversion process with its origins dating back as far as 1860, and it provided the early refining industry with a means of producing desirable, low boiling point hydrocarbons from relatively low-value, heavier stocks.

Over the years since its initial development, the thermal cracking process has found a wide range of uses, and its versatility can be illustrated by mentioning some of the feedstocks it can receive. These may include butane, naphtha, and gas oils, as well as atmospheric and vacuum residues.

The first commercial thermal cracking processes began to appear during the period 1910–1920 as demand for motor gasoline began to expand following the development of the automobile. However, by the early 1920s, it was recognized that gasoline of better anti-knock properties than straight-run material was produced. Thus, apart from increasing the yield of gasoline from crude oil, thermal cracking also gave an improved quality product, and this played an important role in the early development of more efficient, higher compression ratio engines.

By the early 1940s, thermal cracking accounted for over 40 per cent of total motor gasoline production, but soon afterwards began to decline rapidly, and has since been virtually replaced by the more efficient catalytic cracking process. However, adaptations of the thermal cracking process for producing material other than gasoline still remain, and these continue to play an important role in today's refining and petrochemical industry.

The most widely used form of thermal cracking today is the 'steam cracking' process in which straight-run naphtha boiling between 30 and 160°C is converted to a range of low molecular weight olefins, including ethylene, propene, butenes, and butadiene. This process, which is described in more detail elsewhere in this book, is carried out at low hydrocarbon partial pressures obtained by steam dilution, and produces some of the principal building blocks used in petrochemicals manufacture.

Other thermal cracking processes still in common use include 'visbreaking' and 'coking'. Both are used to convert residual oil materials, but whereas visbreaking is carried out under relatively mild conditions as a means of reducing fuel oil viscosities, coking is conducted at high severities to produce distillate products and petroleum coke.

Thermal Cracking Reactions

Depending on feedstock type and product requirement, thermal cracking can be carried out over a wide range of temperatures from 450 to 750°C, and at pressures varying from atmospheric to 70 bars.

Thermal cracking reactions are believed to proceed through the formation of hydrocarbon free radicals. Free radicals are formed by carbon-carbon bond scission, generally towards the centre of a hydrocarbon molecule. For example, a paraffin containing 16 carbon atoms, when subjected to high temperature, may fragment into two free radicals each containing eight carbon atoms.

$$C_{16}H_{34} \longrightarrow \underset{\text{Free radical}}{2CH_3(CH_2)_6\dot{C}H_2}$$

This is often referred to as the initiation reaction. Paraffinic side chains of cyclic hydrocarbons may also form free radicals by a similar reaction, although breakage of carbon carbon bond in an aromatic nucleus is very unlikely to occur.

Unlike the carbonium ions formed in the catalytic cracking process (see later), free radicals carry no electrical charge. They are none the less extremely reactive and rapidly undergo a sequence of further reactions such as cracking to form lower molecular weight hydrocarbons.

Cracking:

$$CH_3(CH_2)_4CH_2.CH_2.\dot{C}H_2 \longrightarrow CH_3(CH_2)_4\dot{C}H_2 + \underset{\text{Ethylene}}{CH_2{=}CH_2}$$

Where secondary free radicals are formed, these may also undergo cracking reactions to form higher molecular weight olefins, e.g. propene, butene, etc. Little or no rearrangement of free radicals, either by hydride or methyl group shift reactions, is believed to occur with thermal cracking, although such reactions are common with catalytic cracking.

$$CH_3(CH_2)_4CH_2.\dot{C}H.CH_3 \longrightarrow CH_3(CH_2)_3\dot{C}H_2 + \underset{\text{Propene}}{CH_2{=}CH.CH_3}$$

$$CH_3(CH_2)_4\dot{C}H.CH_2.CH_3 \longrightarrow CH_3(CH_2)_2\dot{C}H_2 + \underset{\text{n-Butene}}{CH_2{=}CH.CH_2.CH_3}$$

The lower molecular weight free radicals formed as a result of such cracking reactions may themselves continue to crack further until, ultimately, a methyl free radical $CH_3\cdot$ is produced.

A free radical may react with a hydrocarbon by a reaction termed H-transfer to form a new hydrocarbon, generally of lower molecular weight, and another free radical, which is then free to undergo further reaction.

H-transfer:

$$R{-}\dot{C}H_2 + R^1{-}CH_3 \longrightarrow R{-}CH_3 + R^1{-}\dot{C}H_2$$

Addition reactions, in which free radicals react with olefins to form higher carbon number free radicals, are also believed to occur. Where such reactions involve a secondary free radical, some chain branching may take place. However, in general, thermal cracking does not result in a high degree of chain branching in the finished product.

Addition:

$$R{-}\dot{C}H{-}CH_3 + CH_2{=}CHCH_3 \longrightarrow R{-}CH{-}CH_2{-}\dot{C}H{-}CH_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3$$

The free radical so formed, being of higher carbon number, may then re-crack or undergo H-transfer reactions to form lower molecular weight olefins or paraffins.

Eventually, the sequence or chain of free radical reactions is terminated when two free radicals combine to form a new paraffin molecule:

$$R{-}\dot{C}H_2 + R^1{-}\dot{C}H_2 \longrightarrow R{-}CH_2{-}CH_2{-}R^1$$

Although some of the free radical reactions described are exothermic, e.g. addition, the cracking reactions which predominate are endothermic. Hence, the thermal cracking process as a whole is endothermic.

So far, only those reactions involving carbon–carbon bond scission have been described, but under severe thermal cracking conditions, carbon–hydrogen bond scission may also occur. An example of this would be the dehydrogenation of an olefin molecule to form a diene.

Dehydrogenation:

$$CH_2{=}CHCH_2CH_3 \longrightarrow \underset{\text{Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} + H_2$$

Cyclo-paraffins or naphthenes may undergo ring cleavage by the free radical thermal cracking mechanism already described for paraffins. With substituted naphthenes, the relative stability of the side chain will determine the ease of cracking. For example, the stability of naphthenes with paraffinic side chains decreases as the carbon number of the attached side chain increases. Naphthenes may also undergo H-transfer or dehydrogenation reactions, and these will result in the formation of aromatics.

Aromatics are the most refractory, and hence least crackable, class of hydrocarbons. However, with substituted aromatics, dealkylation or fragmentation of the side chain may occur depending on the number of carbon atoms in the side chain.

To summarize, the ease with which the various hydrocarbon types can be thermally cracked decreases in the following order:

Normal paraffins
Iso-paraffins
Cyclo-paraffins
Aromatics
Aromatic/naphthenes
Polynuclear aromatics

Under very severe thermal cracking conditions there is a tendency for coke to form, although the exact mechanism is not entirely understood. It is believed, however, that coke results from the extensive degradation of hydrocarbons to form light gases and polycyclic compounds having very low hydrogen-to-carbon ratios. Such polycyclic materials may take the form of high molecular weight tars or petroleum coke, and are probably the result of fusion of aromatic nuclei by H-transfer or dehydrogenation reactions. Condensation of olefins with polycyclic ring compounds may also play a part in coke formation.

In general, thermal cracking can be considered to be a first order reaction. The rate of cracking is strongly dependent on temperature, and the extent of hydrocarbon decomposition is seen to increase rapidly with temperature.

Cracking reactions start to occur at temperatures of about 315–370°C, depending on the hydrocarbon nature of the material being cracked. The rate of primary decomposition has been observed to double for every 15°C increase in temperature at 440°C and for every 40°C at 600°C.

Pressure also has an important role to play in thermal cracking and determines the phase in which reactions take place. At low pressures (0–6 bars) and high temperatures (above 540°C), reactions occur in the vapour phase, and such conditions favour the formation of the lower molecular weight, lighter hydrocarbons, such as C_2–C_4 olefins.

Higher pressures (15–70 bars), but milder temperatures (400–510°C), result in liquid or mixed-phase operation. Here, the extent of thermal decomposition is less, and depending on feedstock type, this can result in the formation of material boiling in the gasoline or diesel oil range.

Another important variable in thermal cracking is reaction residence time. In general, the greater the reaction time, the lower the temperature required to achieve a given conversion to lighter hydrocarbons. Moreover, long residence times result in an increasing degree of condensation and polymerization reactions, and therefore favour the formation of heavy tars and petroleum coke. Under relatively low temperature conditions long residence times can result in high yields of coke, without producing the excessive volumes of light gases, which are a characteristic of higher severity thermal cracking operations.

Conventional Thermal Cracking

Thermal cracking of higher boiling materials to produce motor gasoline has now become an obsolete process. Fuels with improved anti-knock characteristics (octane number) required for modern automobile engines can now be produced more economically and efficiently by the catalytic cracking process which began to replace thermal cracking in the 1940s.

The majority of thermal crackers operated at temperatures in the range 455–540°C and at pressures between 7–70 bars. The first continuous thermal cracking process was invented by Dubbs in 1913, and was demonstrated commercially in 1919. In this process, a wide boiling range reduced crude was heated to the required temperature in a pipe still before passing to the reaction chamber or soaker drum. Here, thermal cracking occurred to yield a range of products including light gases and gasoline, but leaving a substantial proportion of unconverted material. In later Dubbs units unconverted heavy

distillate was recycled to a second coil in the pipe still to increase the yield of gasoline.

However, one of the major problems with thermal cracking processes was that coke was formed as a by-product. This would deposit within the pipe-still tubes and soaker drum, such that the unit would frequently need to be shut down to carry out decoking operations.

Figure 1 is a flow diagram of a two-coil Dubbs unit. The reduced crude feedstock was first heated by direct exchange with cracked products in the main fractionator. The combined bottoms stream containing feed and some of the unconverted heavy oil then passed to the heavy oil heater, while a gas oil distillate recycle stream was sent to the light oil heater. Due to its more refractory nature, higher temperatures were required to crack the distillate recycle oil.

The two streams from the heater were combined and sent to the soaker drum where additional time was provided to complete the cracking reactions. The cracked products were then separated in a low pressure flash drum from which heavy fuel oil was withdrawn as a liquid. The remaining cracked products would pass as a vapour to the main fractionator for further separation into the required streams. Cracked gasoline and light gases were recovered from the

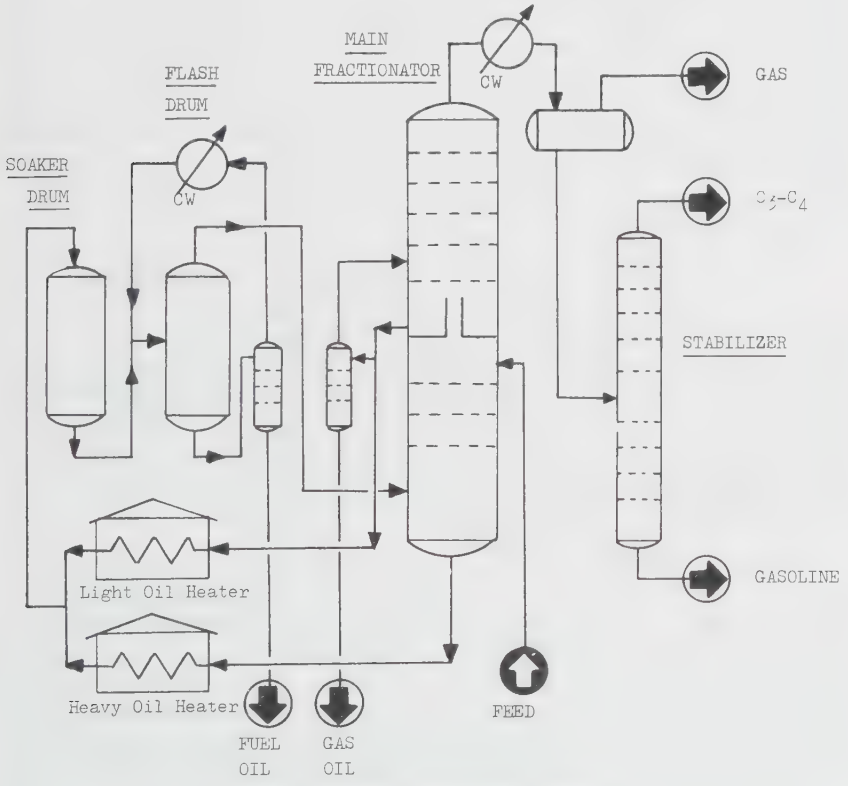


FIG. 1. Dubbs two-coil thermal cracker.

fractionator overheads, and a light heating oil distillate fraction was withdrawn as an upper side-stream.

Typically the heavy oil heating coil would be operated at 500°C and the light oil heating coil at 540°C, with pressure in the soaker drum controlled at 15 bars.

Visbreaking

Visbreaking, or viscosity breaking, is a low severity thermal cracking operation, often used for reducing the viscosity of straight-run residual oils. Normally such residual oils are very viscous and, if required for sale as heavy fuel oil, must be blended with a relatively high-value distillate to meet the finished product viscosity specification. Visbreaking reduces the quantity of distillate required as diluent or 'cutter-stock', and this material can then be diverted to a more profitable outlet, such as diesel oil.

Visbreaking temperatures at the heating coil outlet range from 450 to 500°C, depending on the design of the unit and the nature of the feedstock. Pressures may vary between 4 and 20 bars, but higher pressure is often preferred, since this gives greater control over residence time by minimizing vaporization.

Feedstocks may either be residual oils produced by atmospheric distillation of crude oil and boiling above 350°C, or residues boiling above 550°C obtained by further distilling the atmospheric residue under vacuum. Apart from reducing the viscosity of these residual oils, visbreaking also produces a small yield of light gases and material in the gasoline and gas oil boiling ranges.

Visbreakers have been constructed both with and without soaker drums. Normally units with soaker drums require lower heater outlet temperatures to achieve a given conversion level, and are therefore less prone to coke formation

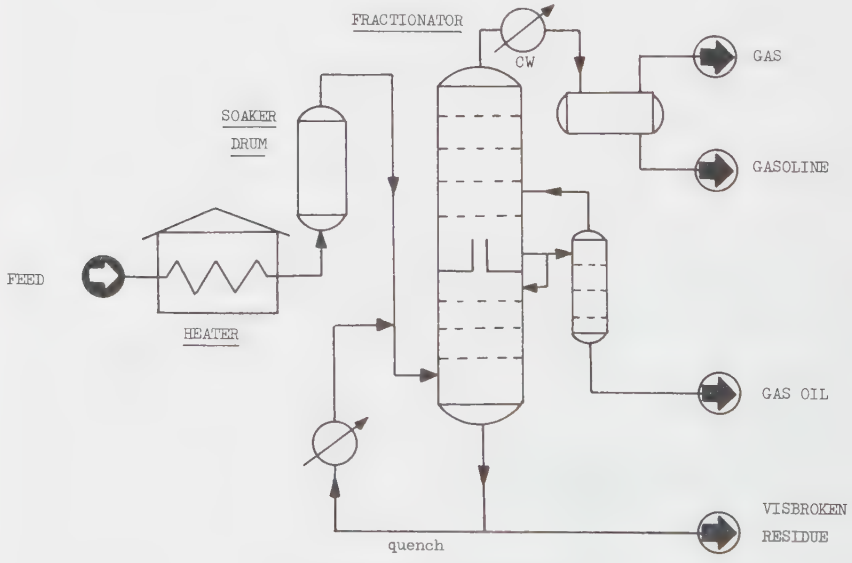


FIG. 2. Visbreaker with soaker drum.

in the furnace coils. However, coke deposits do form in the soaker drum itself and whether a soaker drum is included or not, all visbreakers must be shut down periodically for decoking operations.

A typical visbreaker with a soaker drum is shown in Fig. 2.

Feedstock is heated in the coils of the furnace before passing to the soaker drum, where the desired degree of reaction is accomplished. Soaker drum effluent is then quenched with cool visbroken residue to prevent further cracking in the main fractionator. Gas and gasoline products are recovered from the fractionator overheads, and if required a gas oil fraction suitable for subsequent use as diesel or light heating oil can be withdrawn as a side-cut. Otherwise, this product is allowed to remain in the visbroken residue.

Typical yields for the visbreaking of atmospheric and vacuum residues are compared in Table I.

TABLE I
Visbreaking of Residues

Feedstock	Atmospheric residue	Vacuum residue
Crude source	Kuwait	Iranian light
Density, g/cc	0.970	1.013
Sulphur, % wt	4.1	3.5
Viscosity at 100°C, cS	46	800
Yields, % wt		
Gas	2.5	2.4
C_5–165°C gasoline	5.9	4.6
165–350°C gas oil	13.5	14.5
350°C+ residue	78.1	78.5
Visbroken residue		
Density, g/cc	0.993	1.033
Sulphur, % wt	4.3	3.9
Viscosity at 100°C, cS	25	480

Cracking temperatures used in visbreakers must be carefully controlled to prevent separation of the asphaltenes from the bulk of the visbroken residue product. These asphaltenes are normally held in colloidal suspension by complex peptizing agents which occur naturally in crude oil. Under severe cracking conditions these peptizing agents tend to be destroyed and the asphaltenes precipitate, thereby rendering the visbroken residue unsuitable for sale as fuel oil. This problem is usually referred to as fuel oil instability.

Combination Cracking

Combination cracking is a higher severity form of visbreaking for maximizing gas oil yield from atmospheric residue feedstocks. In this process a heavy fraction boiling between 350 and 500 °C, obtained by distilling the visbroken residue under vacuum, is recycled to a second furnace coil for further cracking.

The primary furnace coil is operated under the relatively mild conditions typical of visbreaking. However, higher temperatures are required to crack the recycle oil in the secondary coil. Fortunately the recycle stream does not

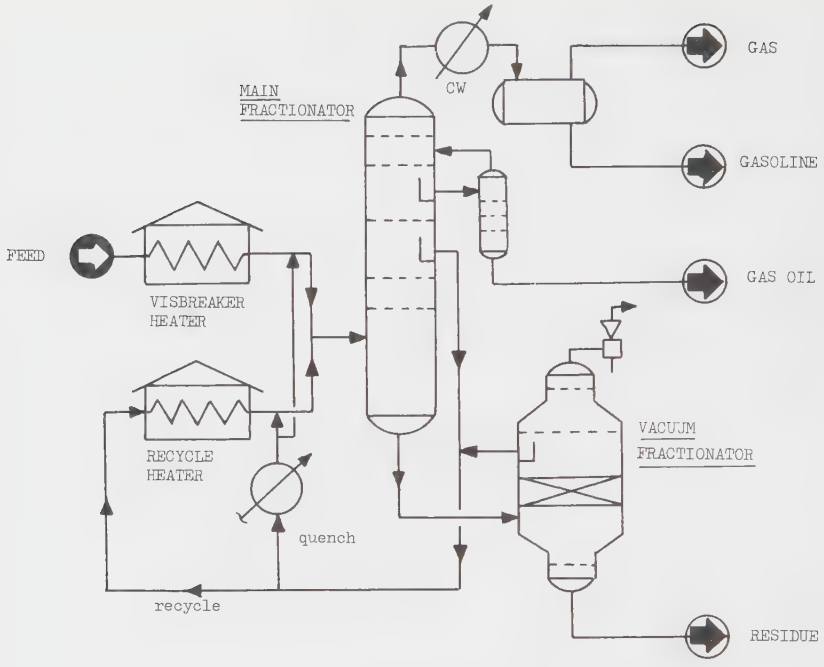


Fig. 3. Combination cracker.

contain the all-important peptizing agents, so the higher overall severity of this process does not lead to fuel oil instability causing asphaltenes precipitation.

A flow scheme for a combination cracker is depicted in Fig. 3, while typical yields are given in Table II.

Coking

Coking processes are relatively severe cracking operations designed to convert residual oil products, such as straight-run atmospheric and vacuum residues, tars and pitches, into more valuable lighter products, such as naphtha and diesel oil. In addition, gas and coke are produced. The yield of each product is

TABLE II
Combination Cracking Yields

Feedstock	
Density, g/cc	0.955
Sulphur, % wt	2.5
Viscosity at 100°C, cS	30
Yields	
Gas	4.0
C_5–150°C gasoline	7.5
150 350°C gas oil	35.6
350°C+ residue	52.9

dependent on the coking conditions and the quality of the feedstock fed to the process.

The C_5–180°C naphtha may be used, following hydrotreatment, as a petrochemical feedstock, or after splitting into C_5–80°C and 80°C–180°C fractions as a gasoline blending component and catalytic reformer feedstock, respectively.

The 180°C–330°C gas oil fraction, also after hydrogenation, can be a suitable automotive diesel component if derived from a more paraffinic type feedstock, or alternatively can be used as a heating oil.

The heavy gas oil fraction (330°C upwards) may be used as a fuel oil blending component, fluid catalytic cracker feedstock or, after further processing, as a needle coke feedstock.

The coke produced from suitable feedstocks may be used for electrode manufacture and the production of chemicals, thus considerably increasing its value. Otherwise this material is used as a fuel.

With the current diminishing demand for fuel oils, coking processes are being examined again to see if they will meet individual refiner's requirements. Several large cokers are currently being constructed, particularly in the United States.

There are two main types of coking process available, namely, delayed and fluid coking. The latter process has further been developed into a process known as flexicoking, whereby the fluid coke produced is gasified to produce low thermal value gas.

Delayed Coking

Delayed coking can be described as a semi-continuous process in which the feedstock to the process is heated to a high temperature at high velocity, and then transferred to a large drum which allows for the long residence time required for the cracking reactions to proceed to completion, thereby depositing the coke in the drum.

Figure 4 shows a simplified flow diagram of a delayed coking unit operating on a straight-run atmospheric residue feedstock. The feed is charged to the base of the main product fractionator after heat exchange with coker distillate products. The feed, and a recycle stream of heavy coker distillate, are then heated in a specially designed furnace to a temperature in the range of 480 to 515°C at the furnace outlet. The heated oil then passes to one of a pair of coking drums. The cracked products leave from the top of the drum, whilst the coke formed is deposited in the drum. To maintain continuous operation, two or more coke drums are used. Whilst coke is being deposited in one drum, the other drum is emptied. As the cracking reactions are endothermic the temperatures in the coke drum are lower than at the furnace outlet and usually are in the range 415 to 460°C. Drum pressure varies from 1 bar (g) up to about 7 bars (g).

The cracked products pass to a large fractionation tower, where gas, naphtha, and gas oil fractions are removed as products. Heavy distillate products may be recycled with fresh feed for recracking.

The heart of the coking process is the coker furnace, and the design has been modified in recent years to give longer run lengths before decoking of the

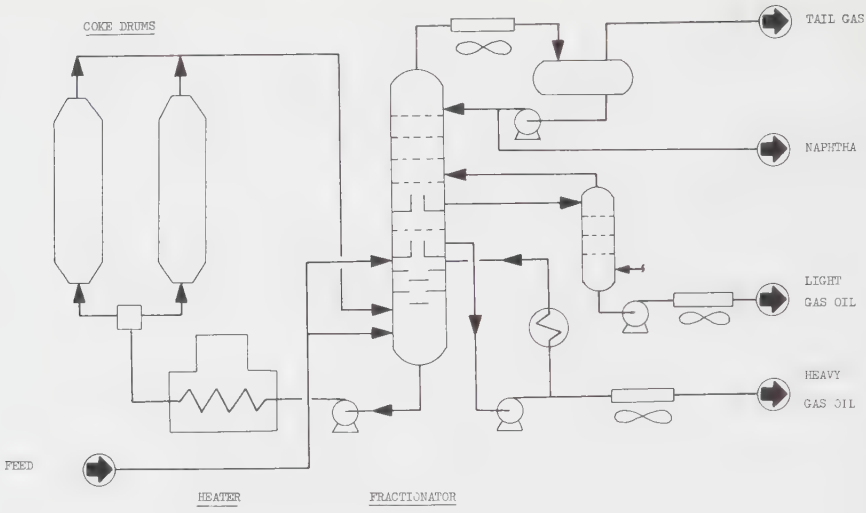


FIG. 4. Delayed coking unit.

furnace tubes becomes necessary. Cold oil velocities are now about 2 m/sec, and multiple injection of steam into the heater coil is practised to adjust coil residence time and velocity. Heat flux rates are being reduced to 25 000 kcal/m^2/h from the traditional values of 28 32 000 kcal/m^2/h.

The main process variables in delayed coking are:

1. Feedstock type. Feedstock quality as measured by the UOP K-factor, can affect the yield of coke and the quality of the distillate products. The lower the UOP K-factor, the more aromatic the feed and the more aromatic the final products. The coke yield is dependent on the Conradson carbon content of the feedstock, high values giving higher yields of coke.
2. Recycle ratio, which is defined as the (fresh feed + recycle feed)/fresh feed, can vary from 1.1 to nearly 2.0. The higher the recycle ratio, the greater the coke yield from a given feedstock. Furthermore, more naphtha and less heavy gas oil are produced, and the overall liquid yield decreases.
3. Drum pressure. Increase in coke drum operating pressure retains more of the heavy hydrocarbons in the coke drum. This increases the coke yield. It also results in slightly increased gas yields, whilst decreasing the overall liquid produced. The effect of pressure is shown in Table III.

The coke drum is usually sized to be on stream for 24 h before becoming full of 'green' coke. After switching feed to the second drum, the following procedure is used to remove coke from the drum:

(a) The coke drum is first depressured and steamed out to remove uncondensed vapours, which are sent to a blowdown drum via the fractionator.
(b) The drum is then filled with cold water to cool the coke down. Steam generated, plus hydrocarbon vapours, pass to the blowdown drum.

TABLE III
Effect of Pressure on Delayed Coking Yields

Feedstock		
Crude source		Wilmington
TBP cut point		550°C
Specific gravity at 15/15°C		1.054
Conradson carbon		20.6% wt
Sulphur		2.4% wt
Estimated yields at constant recycle ratio		
Drum pressure	1 bar (g)	2.4 bars (g)
Dry gas (inc. C_4), % wt	16.1	16.5
C_5–193°C naphtha, % wt	12.0	12.4
Specific gravity at 15/15°C	0.793 6	0.792 3
Sulphur, % wt	1.4	1.3
193°C+ gas oil, % wt	37.3	33.3
Specific gravity at 15/15°C	0.940 2	0.935 2
Sulphur, % wt	1.8	1.8
Coke, % wt	34.6	37.8
Sulphur, % wt	2.4	2.4

(c) The water is drained down and the top and bottom heads of the coke drum are removed to permit emptying.
(d) A hole is drilled through the centre of the coke deposit using a high pressure water jet.
(e) The coke is then removed by cutting out the depósits with multiple high pressure water jets spraying radially from the centre of the drum.

The coke dropping out of the base of the drum is accompanied by large volumes of drilling water. Many different coke dewatering/handling systems are available, the most common being:

direct rail-car loading
pad or apron loading
pit loading
and dewatering bins.

Direct rail-car loading is the cheapest, but has the disadvantage that decoking is dependent on the time for rail-car movement.

Pad loading allows the coke water to flow from the drum through a chute on to a concrete apron. The water drains to the periphery of the pad into a settling maze where coke fines settle out before the clear water is recycled to the decoking water surge tank for re-use. The coke is removed from the pad by a front-end loader or an overhead crane.

Pit loading is very similar to pad loading, except that the coke empties into a concrete pit instead of a concrete apron. An overhead crane is required for coke handling.

Dewatering bins have evolved to provide totally enclosed systems to meet exceptional environmental requirements or to prevent coke contamination in areas where sand storms may be a problem.

Delayed coker design has been modified over the years to meet mounting environmental concern. One example is the need for the blowdown facilities mentioned above. Blowdown systems did exist for the recovery of wax tailings

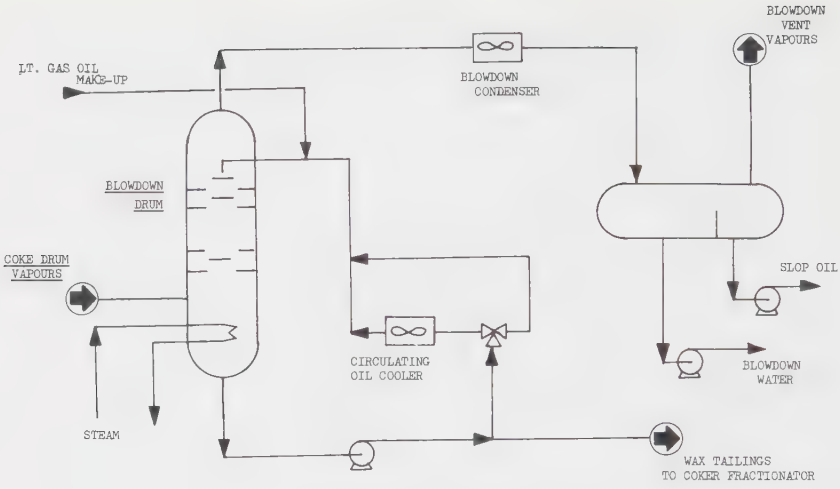


FIG. 5. Typical delayed coker blowdown system.

and the condensation of steam. However, non-condensable vapours were water scrubbed and vented to atmosphere. A typical modern system is shown in Fig. 5. The vent vapours pass to the flare or may be recovered using a vent gas compressor.

Typical yields and product properties for a range of different feedstocks are shown in Table IV.

Cokes produced from delayed coking can be used for a number of different applications. The limiting quality factors for each of the major coke markets are summarized in Table V.

TABLE IV

Typical Delayed Coking Yields at Constant Recycle Ratio and Drum Pressure

Feedstocks					
Crude source	Brega	Orinoco	Alaskan	Arab. Lt	Arab. Hy
TBP cut point, °C	560	510	565	565	565
Specific gravity, 15/15°C	0.984 0	1.055 2	1.008	1.109	1.040
Conradson carbon, % wt	14.6	23.3	16.1	15.4	24.2
Sulphur, % wt	1.06	4.40	2.16	4.1	5.25
Products					
Dry gas (inc. C_4), % wt	7.0	16.3	11.3	11.1	13.2
C_5–193°C naphtha, % wt	18.6	16.2	14.6	16.1	13.5
Specific gravity, 15/15°C	0.736 2	0.779 6	0.748 3	0.743 6	0.756 3
Sulphur, % wt	0.11	1.25	0.70	1.00	1.11
193°C+ gas oil, % wt	52.4	29.6	47.6	45.8	40.4
Specific gravity, 15/15°C	0.846 3	0.941 5	0.903 6	0.886 6	0.895 6
Sulphur, % wt	0.83	4.10	1.40	2.30	2.40
Coke, % wt	22.0	37.9	26.5	27.0	33.0
Sulphur, % wt	1.9	4.3	3.0	6.4	7.1
Ni + V, ppm wt	182	3700	607	366	676

TABLE V
Petroleum Coke Market Specifications

Grade	Sulphur	Metals
Fuel	Regional limits	None
Metallurgical	Limiting	None
Anode	Limiting	Limiting
High purity reactants	Limiting	Limiting

Premium quality 'green' coke (low sulphur and low metals) is traditionally calcined for the production of amorphous carbon anodes used in the manufacture of aluminium. The critical parameters for this application are given in Table VI.

It is evident from Table IV that cokes produced from selected crudes can be used for anode production.

Fluid coking

Fluid coking is a continuous process, first introduced to the refining industry in 1954, which uses the fluidized solids technique to convert residue feedstocks to more valuable products. The residue is coked by spraying into a fluidized bed of hot, fine coke particles. The use of a fluid bed permits the coking reactions to be conducted at higher temperatures and with shorter contact times than in delayed coking. These conditions result in lower yields of coke and higher yields of liquid products. Fluid coking uses two vessels, a reactor and a burner. Coke particles are circulated between these to transfer heat to the reactor. This heat is generated by burning a portion of the coke. A schematic flow diagram of a fluid coker is given in Fig. 6.

The reactor contains a fluidized bed of coke particles, which is agitated by the introduction of steam below. The residue feed is injected directly into the reactor and is distributed uniformly over the surface of the coke particles where it cracks and vaporizes. No preheat is necessary as the circulating coke particles supply the heat required for the coking reaction and control of the reaction temperature. Vapour products leave the bed and pass through cyclones which remove most of the entrained coke. The vapour is then discharged into the

TABLE VI
Typical Aluminium Anode Coke Specification

Coke	Green	Calcined
Volatiles, % wt	12 (max)	0.5–0.6 (max)
Metals, ppm		
Silicon	200–300 (max)	200–300 (max)
Iron	300 (max)	300 (max)
Vanadium	200–250 (max)	200–250 (max)
Other metals	300 (max)	
Sulphur, % wt	2.5–4.0 (max)	2.5–3.0 (max)
Real density, g/cc		2.0 (min)

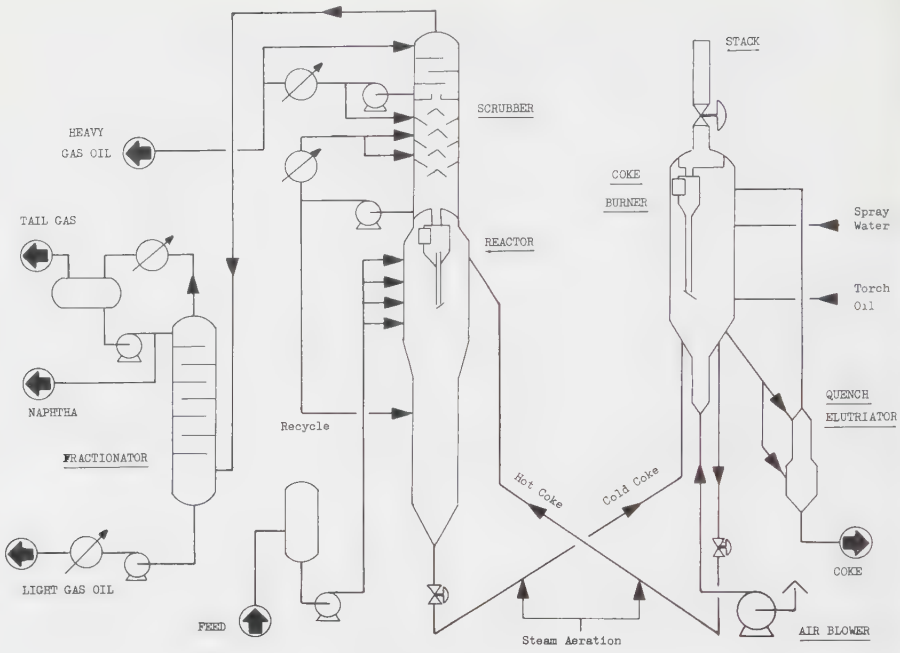


FIG. 6. Fluid coking process.

bottom of the scrubber where the remaining coke is removed and the products cooled to condense the heavy tar. The resulting slurry is recycled back to the coking reactor. The overhead products from the scrubber are sent to fractionation for separation into gas, naphtha, light and heavy gas oils.

The coke particles in the reactor vessel flow down into a stripping zone at the base where stripping steam removes any product vapours from between the coke particles. The coke then flows down a stand-pipe and into a riser which leads to the burner. Steam is used to induce upward flow of the coke into the burner.

The average bed temperature in the burner is maintained by adding air as required to burn part of the product coke.

Typical operating conditions in the reactor and burner are as follows:

	Reactor	*Burner*
Temperature, °C	510	620
Pressure, bar (g)	0.7	0.75
Velocity, m/sec	0.3–0.9	0.6–0.9
Bed depth, m	9–15	3–4.5

Flue gases from the burner bed pass through cyclones and discharge to a stack through a variable orifice to control burner pressure. Hot coke is returned to the reactor through a second stand-pipe and riser assembly.

As coke is one of the products of the process, it must be withdrawn from the burner bed to prevent the solids inventory from increasing. To prevent the circulating coke from becoming too coarse, large particles are removed through

TABLE VII
Typical Yields on Fluid Coking

Crude source	Atmospheric residues		Vacuum residues	
	South Louisiana	Zaca	South Louisiana	Hawkins
Feedstock				
Specific gravity, 15/15°C	0.948	1.039	0.978	1.043
Conradson, carbon, % wt	5.0	19.0	14.0	24.0
Sulphur, % wt	0.5	7.8	0.9	4.3
Yields on coker feed				
C_3 and lighter, % wt	6	8	8	9.5
C_4, % vol	2	2.5	2.5	3.5
C_5–220°C, % vol	17	20.5	21.5	19.5
220–545°C, % vol	74	61	61	52
Coke (gross), % wt	8	17.5	16	27.5
Product quality				
Naphtha (C_5–220°C)				
Specific gravity, 15/15°C	0.755	0.784	0.755	0.755
Sulphur, % wt	0.1	4.6	0.2	0.9
Gas oil (220–545°C)				
Specific gravity, 15/15°C	0.910	0.973	0.922	0.953
Sulphur, % wt	0.4	6.2	0.5	3.7
Nitrogen, % wt	0.13	0.41	0.20	0.12
Characterization factor	11.81	10.90	11.55	11.17

a quench elutriator drum and replaced with smaller seed particles. Normal coke circulation from the coke burner is in the range 5–10 kg/kg of feed. The cooled coke removed from the system is usually in the 20 200 mesh size range.

Typical yield and product data on a range of feedstocks are given in Table VII.

Flexicoking

Flexicoking is a recently developed extension of the fluid coking process. A schematic diagram of the process is shown in Fig. 7.

The process employs three major vessels: a reactor, a heater, and a gasifier. The coke produced in the reactor passes through the heater where it is partially devolatilized before passing to the gasifier. In the gasifier, the coke reacts at elevated temperatures with air and steam to form a mixture of carbon monoxide, carbon dioxide, hydrogen, nitrogen, water vapour, and hydrogen sulphide. The gas produced in the gasifier passes through the heat exchanger, where it is cooled to provide part of the reactor heat requirement. The remainder of the heat is supplied by circulating coke between the gasifier and the heater.

The cooled coke gas leaves the heater and is further cooled in a waste-heat boiler. Entrained coke dust is removed and the gas desulphurized using conventional processing. The resulting product is a clean low calorific value fuel gas (800–1150 kcal/m^3), suitable for use as a fuel in boilers or process furnaces.

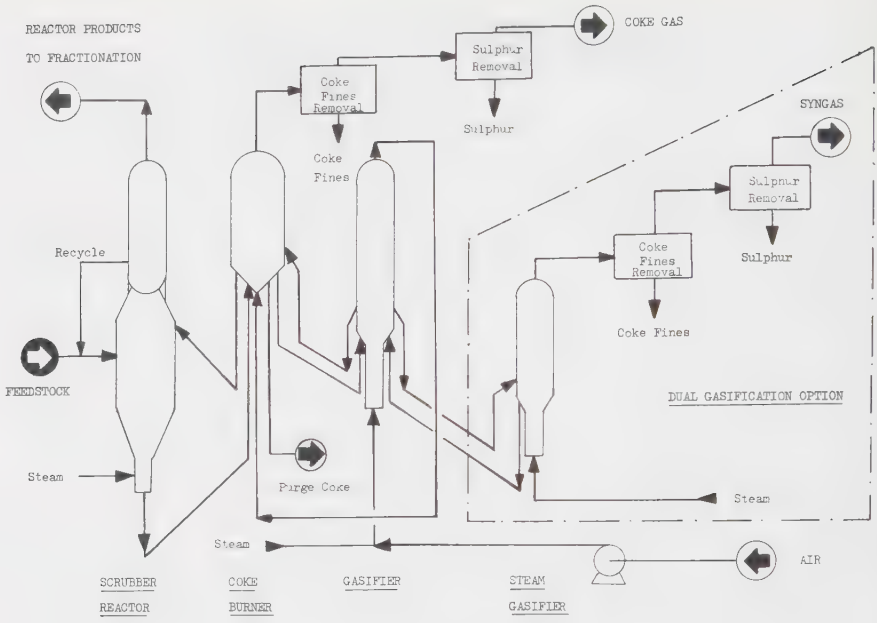


FIG. 7. Flexicoking process.

The first commercial unit was started up in Japan in 1976, and feed rates of 110-115 per cent of design have been demonstrated with 97 per cent of the gross coke converted to gas.

Typical product and gas yields with three different feedstocks are given in Table VIII.

TABLE VIII
Flexicoker Feedstock Flexibility

Feedstock Crude source	Athabasca bitumen*	Boscan	West Texas sour asphalt†
Specific gravity, 15/15°C	1.0057	1.0328	1.0777
Conradson carbon, % wt	13.0	18.0	34.0
Sulphur, % wt	4.8	5.2	4.6
Nitrogen, % wt	0.4	0.76	0.65
Nickel and vanadium, ppm	350	1295	137
Product yields, % wt			
H_2S	1.0	1.0	1.2
C_1–C_3	5.4	7.8	10.1
C_4	1.7	1.6	2.2
C_5–220°C	13.1	12.7	12.3
220–525°C	63.7	54.8	30.4
Coke	0.8	1.1	2.0
Coke gas, FOEB Basis‡	(7.1)	(11.8)	(30.0)

* Feed properties and yields on solids free basis.
† Asphalt from propane de-asphalting of West Texas sour residue.
‡ FOEB = Fuel Oil Equivalent Barrel.

TABLE IX

Vacuum Distillation Unit/Coker Reactor Yield Comparison Arabian Heavy 565°C+ Feedstock

	Base case	Integrated case
Recycle cut point, °C	525	565
Product yields		
H_2S, % wt	1.4	1.2
C_1–C_4, % wt	11.9	10.7
Naphtha (C_5–177°C), % vol	17.3	16.4
Light gas oil (177–371°C), % vol	19.6	15.9
Heavy gas oil (371–525°C), % vol	24.0	21.7
Very heavy gas oil (525–565°C), % vol	—	9.7
Total liquid products, % vol	60.9	63.7
Nett coke, % wt	0.93	0.87
Low calorific value gas (dry), m^3/m^3	1 900	1 760

More recently, further changes have been made to increase the attractiveness of the flexicoking process.

1. Integration of the Flexicoker reactor with the upstream vacuum distillation unit to raise the effective cut point between the coker gas oil and the slurry oil recycled to the reactor from 525°C to about 565°C. A comparison of product yields with the standard case is shown in Table IX.
2. Dual gasification of the coke to reduce the production of low calorific value coke gas. Air and steam gasification steps are carried out in separate vessels such that synthesis gas and/or hydrogen can be produced directly. In the air gasifier coke is burnt to provide reaction heat for the reactor and the steam gasifier, with resulting production of low calorific value gas. In the steam gasifier, a hydrogen–carbon monoxide rich gas, free of nitrogen, is produced, which can be passed through shift reactors for hydrogen manufacture, or used as syngas for chemicals manufacture.

CATALYTIC CRACKING

Introduction

Catalytic cracking has, without a doubt, become the major process in the petroleum refining industry for producing gasoline from heavy oils and, today, is the most important means for increasing the ratio of light to heavy products from crude oil. Large-scale construction of catalytic crackers began in the 1940s and this process very quickly superseded thermal cracking for gasoline production due to its higher yields and improved product qualities.

The catalytic cracking process was developed from a discovery by Houdry in 1927 that certain naturally occurring silica-alumina clays catalysed the cracking of high molecular weight hydrocarbons to give a good yield of gasoline. The catalyst, however, quickly became coated with a layer of coke, which blocked the catalytic sites and reduced its cracking activity. This could

be restored by carefully burning off the coke in a stream of air, and the regenerated catalyst could then be used for a further processing cycle.

The first catalytic cracking plants were built in the USA in the period from 1930 to 1940. These used multiple fixed bed reactors which had to be periodically switched from cracking to regeneration duty to maintain catalyst activity. No real advance was made, however, until methods of continuously processing and regenerating the catalyst were developed. Two systems evolved, namely the moving bed and fluidized bed processes. In the moving bed process the catalyst is allowed to fall slowly by gravity through the reactor and regenerator vessels before being returned mechanically to the top of the reactor. The fluidized bed process, on the other hand, is based on the fluidization properties of the fine powders, which enable the catalyst to be transported continuously between the reactor and regenerator at extremely high flow rates. Of the two systems developed, the fluidized bed process has been the most widely used and, today, represents over 95 per cent of all cracking plant. All modern cracking units are of this type.

Although the methods used for transporting catalyst in the two processes are fundamentally different, the principles of reaction and catalyst regeneration are similar. Both take place at pressures only slightly above atmospheric, up to 2.5 bars (g), and at temperatures in the range of 480–540°C for reaction and 630–760°C for regeneration.

Catalytic Cracking Reactions

The reactions which take place in the catalytic cracking process are complex, and are further complicated by the diverse range of hydrocarbon types present in the feedstock. However, the following order of increasing reactivity has been observed for hydrocarbons having the same carbon number:

Unsubstituted aromatics
Paraffins
Polymethylaromatics
Naphthenes
Alkylbenzenes (with side chains greater than C_3)
Olefins

Furthermore, reaction rates increase with increasing molecular weight for all classes of hydrocarbon.

Unlike the thermal cracking process, which involves a free radical chain reaction mechanism, catalytic cracking proceeds through the formation of carbonium ions. These are formed as intermediates in catalytic cracking reactions and are defined as being electron-deficient groups containing a positively-charged carbon atom. Carbonium ions are formed in the presence of an acidic catalyst, either by the removal of a hydride ion from a saturated hydrocarbon or by the addition of a proton to an olefin or aromatic nucleus.

$$\underset{\text{Paraffin}}{R{-}CH_2{-}CH_2{-}CH_3{-}H^-} \longrightarrow \underset{\text{Carbonium ion}}{R{-}CH_2{-}\dot{C}H_2{-}CH_2}$$

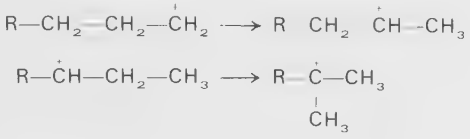
In order to produce carbonium ions the catalyst system must, of course, be capable of either accepting an electron pair, or donating a proton.

Carbonium ions are highly reactive and have only a transient existence, but are responsible for almost all of the reactions which occur in the catalytic cracking process. The ease with which they are formed depends on their relative stability which decreases in the order:

tertiary > secondary > primary > ethyl > methyl

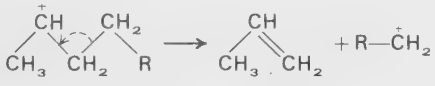
Once formed, carbonium ions rapidly undergo a number of reactions which are discussed below:

Isomerization. Rearrangement by 1,2-hydride or methyl group shift reactions occurs whenever this will result in an increase in carbonium ion stability. For example, a primary carbonium ion will tend to isomerize to a secondary carbonium ion, which in turn may be transformed into the more stable tertiary form.



This reaction explains the high concentration of branched chain hydrocarbons in catalytic cracker products, and is one of the major differences compared with thermal cracking.

β-scission. Cracking of carbonium ions occurs at the C –C bond which is located in the β position relative to the carbon atom carrying the positive charge.



Reactions of this type explain the relatively high yields of propene, butene, pentene, and higher olefins in catalytic cracker products. However, due to the relative instability of primary carbonium ions and their rapid isomerization to the secondary or tertiary forms, the yield of ethylene by this reaction is very low.

The new carbonium ion, formed as a result of a β-scission reaction, continues to isomerize and crack according to the reactions already described until further cracking would result only in the formation of the highly unstable methyl or ethyl carbonium ions. At this point β-scission stops, and the remaining carbonium ion, which might contain only four or five carbon atoms, is then destroyed by hydrogen transfer with another molecule.

Hydrogen transfer. At any point in the sequence of isomerization and cracking reactions just described, a carbonium ion can undergo hydrogen transfer reactions with other molecules. For example, it can abstract a hydride ion from a paraffin to form a new carbonium ion.

Alternatively, it may donate a proton to an olefin to give a different olefin and carbonium ion.

$$CH_3—\overset{+}{C}H—CH_3 + C_4H_8 \longrightarrow CH_3—CH{=}CH_2 + C_4H_9^+$$

Termination. To complete its reaction sequence, a carbonium ion is finally destroyed by abstracting a hydride ion from, or donating a proton to, the acid site on the catalyst.

As already described, the major cracking reaction for paraffins is carbon–carbon bond scission to form lighter paraffins and olefins. Unlike thermal cracking, catalytic cracking results in a high degree of isomerization, and the yields of methane, ethane, and ethylene are relatively low. In catalytic systems, normal paraffins crack between five and 60 times faster than in non-catalytic systems. Isoparaffins, in turn, crack more rapidly than normal paraffins of the same carbon number.

Olefins are the most reactive class of hydrocarbons in catalytic cracking. Once formed, they tend to crack rapidly at rates between 1000 and 10 000 times greater than are found in thermal cracking. Under severe cracking conditions with low acidity catalysts, the higher boiling point olefins are almost completely converted to low carbon number olefins (C_3–C_5) in the LPG and light gasoline boiling ranges.

Olefins also undergo rapid isomerization, by both hydride and methyl group shift reactions, to produce a mixture of isomers in which the distribution of double bonds and the degree of chain branching approach thermodynamic equilibrium. Tertiary olefins formed as a result of such reactions are extremely reactive and, with a strongly acidic catalyst, undergo hydrogen transfer reaction with naphthenes or other hydrocarbons, e.g.

$$\underset{\text{Olefins + Naphthene}}{3C_nH_{2n} + C_mH_{2m}} \longrightarrow \underset{\text{Paraffins + Aromatic}}{3C_nH_{2n-2} + C_mH_{2m-6}}$$

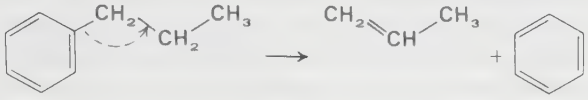
This reaction is believed to proceed through the abstraction of hydride ions from the naphthene molecule by the catalyst and their subsequent transfer to olefinic carbonium ions. Tertiary olefins are thus converted into isobutane and high octane number isoparaffins in the gasoline boiling range. This accounts for the very high iso/normal paraffin ratios observed in catalytic cracker products, ratios which can greatly exceed equilibrium expectations.

Undoubtedly, the most important result of hydrogen transfer is that it stabilizes or preserves gasoline boiling range olefins formed by primary cracking of gas oil, prior to their cracking further to C_3–C_4 by secondary reactions.

Another consequence of hydrogen transfer is the formation of aromatics. Further hydrogen transfer may result in the condensation of aromatic nuclei to form complex polynuclear materials which are no longer volatile under the conditions of the reactor. This is believed to be one of the reactions responsible for coke forming on the catalyst surface. The coke produced by catalytic cracking in fact consists of hydrocarbon with a very low hydrogen-to-carbon ratio (approximately 6 8% wt hydrogen).

Naphthenes, due to their greater number of secondary and tertiary carbon atoms, crack more readily than the corresponding straight-chain paraffins, but less readily than olefins. Naphthene cracking occurs by both ring and side chain rupture to produce light olefins and paraffins. Again, the formation of methane and C_2 hydrocarbons is relatively low.

Alkylbenzenes with side chains containing two or more carbon atoms undergo de-alkylation reactions to form benzene and the corresponding olefin, e.g.



De-alkylation may also be responsible for the small yield of methane found in catalytic cracker off gases. The aromatic nucleus itself is almost inert, although there is some evidence that condensed rings such as naphthenes, phenanthrene, and anthracene do crack slowly. When this occurs, coke is the major product.

The hydrogen found in catalytic cracker products comes from the direct dehydrogenation of hydrocarbons and, in particular, from material converted into coke by condensation reactions. The presence of metals contaminants, especially nickel, greatly accelerates hydrogen formation.

Catalyst

The catalysts used in both the moving bed and fluidized bed systems are basically very similar, although produced in a different form. Whereas the moving bed uses catalyst in the form of beads, the fluidized bed system requires finely powdered catalyst.

Early catalysts consisted of synthetic amorphous silica-alumina containing between 13 and 27% wt alumina. These have now been replaced by catalysts containing a proportion of synthetic aluminium silicate zeolite, which have greater activity due to their stronger acidity. Such catalysts result in higher levels of conversion to more valuable products, and because of their enhanced hydrogen transfer activity, suppress the secondary cracking of gasoline components to light olefins.

Zeolite is manufactured by reacting sodium aluminate in the correct stoichiometric ratio under carefully controlled conditions of temperature, pH, and residence time. The zeolite, which forms as a precipitate, has a well defined crystalline structure, and consists of an inorganic polymer containing AlO_4 and SiO_4 tetrahedra. These tetrahedra are linked by shared oxygen atoms and, because trivalent aluminium atoms occupy some of the positions of tetravalent silicon, the zeolite itself is anionic in nature. When initially produced, the zeolite contains sodium cations, but in this form it possesses little or no catalytic activity. However, one of the properties of zeolites is that cations can be readily replaced with other cations by a process termed ion-exchange.

In the next stage of catalyst manufacture, the sodium ions are commonly exchanged with rare earth cations (lanthanum, cerium, neodymium, etc.) to form a zeolite which exhibits the required acidic activity. Alternatively, exchange may be carried out with ammonium cations and, on subsequent

drying at a high temperature, ammonia is driven off to produce an active zeolite in the hydrogen form.

Unfortunately pure zeolite is too active and does not have the required mechanical strength for direct use as a cracking catalyst, and so must be dispersed in a relatively inactive, amorphous silica alumina matrix. This can be carried out by mixing the zeolite crystals with a silica–alumina hydrosol or hydrogel to which may have been added a proportion of naturally occurring clay, such as kaolin, as filler.

In the manufacture of bead catalysts for the moving bed process, prepared hydrosol is passed over a fluted cone to produce large droplets, which are then allowed to fall through a column of hot oil. The hydrosol droplets set to form beads of about 8 mm diameter and, after drying at 175 °C, these shrink to a final diameter of about 3 mm.

Catalysts used in the fluid catalytic cracking process are prepared by spray-drying the final hydrogel or hydrosol under carefully controlled conditions to produce micro-spheroidal particles of the required particle size distribution. Typical properties of fresh and equilibrium (used) fluid cracking catalysts are given in Table X. This shows that pore shrinkage occurs in use, leading to a reduction in surface area (and activity) and a corresponding increase in bulk density.

Fluid Cracking

Following the commissioning of the first fluid catalytic cracking unit by Standard Oil of New Jersey (Esso) in 1941, this process soon assumed the dominant role in the refining industry for converting heavy fuel oil distillates into more valuable lighter components, notably motor gasoline. The fluid cracking process has continued to evolve and its efficiency has greatly improved as a result of many technical innovations and the development of more active catalysts. Of particular importance was the introduction of zeolites in the late 1960s, which greatly increased the conversion to gasoline.

TABLE X
Properties of Fluid Cracking Catalysts

	Fresh	Equilibrium
Chemical analysis, % wt:		
Al_2O_3	31.0	31.0
Na_2O	0.65	0.65
SO_4	0.20	—
Fe	0.15	0.50
Rare earth oxides	3.0	3.0
SiO_2	balance	
Surface area, m^2/g	155	80
Pore volume, cm^3/g	0.20	0.15
Apparent bulk density, g/cm^3	0.79	0.92
Particle size distribution, % wt		
0–20 microns	2	1
20–40 microns	15	7
40–80 microns	50	61
Average particle size, microns	64	68

The basis of the process is the fact that finely divided powders behave like a fluid when aerated with a gas. A bed of cracking catalyst of about 60 microns average particle size is 'fluidized' at upward gas velocities of 60–100 cm/sec, and in almost all respects acts like a fluid with a density of 0.40–0.65 g/cm^3. In this state, catalyst can easily be made to flow down pipes, for example, from one vessel to another. As gas velocity is increased, the finer catalyst particles are elutriated from the bed, and at velocities exceeding 3 m/sec, the entire catalyst is transported by the gas stream. Hence, by selection of high velocities, catalyst can also be made to flow through pipes in an upward direction. These are basically the principles by which catalyst is transferred between the reactor and regenerator vessels on a fluid catalytic cracker. Catalyst circulation rates 5–8 times greater than the feed rate to the unit are necessary, and this is only possible because of the fluid behaviour of the catalyst.

The desirable properties of fluidized systems can be attributed to the intense agitation and mixing caused by rapidly moving catalyst particles. High mass-transfer rates between the catalyst surface and the gas phase help to increase reaction rates. Moreover, high heat-transfer rates are possible between the catalyst particles and gas phase, and between different points in the fluid bed, which means that a fluid bed can be used as an isothermal reactor. This characteristic makes the fluidized system particularly suitable for processes in which large quantities of heat are released or absorbed.

Numerous catalytic cracker designs have appeared over the years as a result of work by Kellogg, UOP, Esso, Gulf, Texaco, and others, but essentially these can be broken down into the following sections:

Reactor/regenerator
Flue gas energy recovery
Fractionation
Gas concentration

Until the early 1970s, all designs used a reactor containing a bed of fluidized catalyst. However, with the introduction of high activity catalysts, it was found that only very short hydrocarbon/catalyst contact times were required to achieve the desired level of conversion. Indeed, extended contact times often resulted in undesirable secondary reactions, and excessive gas and coke production.

This led to the development of the modern short contact time reactor system in which the cracking reactions are carried out entirely in the catalyst transfer line, or riser.

Figure 8 shows a typical reactor/regenerator layout designed by Universal Oil Products. Feedstock, preheated to 250–400°C, contacts hot regenerated catalyst in the base of the reaction riser. Very rapid heat transfer and vaporization of the feed occur at this point, and the resultant high velocity is sufficient to transport the catalyst to the top of riser, where separation from the hydrocarbon products takes place. Spent catalyst, containing about 1% wt coke, collects in the base of the reactor and passes through the stripper where entrained hydrocarbon vapours are removed by a counter-current flow of steam. On entering the regenerator, the catalyst is fluidized with air and the coke is burnt off. Regenerated catalyst then flows through a control valve to the base of the riser to complete the cycle.

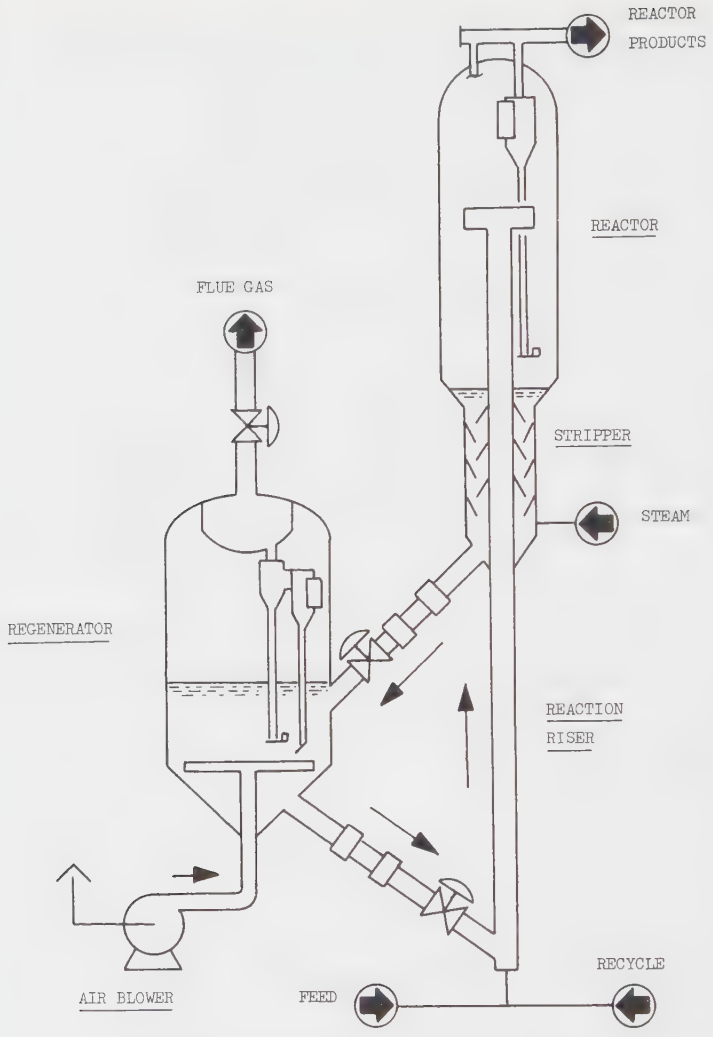


FIG. 8. Typical UOP reactor/regenerator layout.

Cyclone separators, usually in two stages, are used in both the reactor and regenerator to remove as much as possible of the entrained catalyst from the outgoing vapours. Reactor product vapours pass to the fractionation and gas concentration section, whilst flue gas after energy recovery leaves via the stack. Abrasion-resistant refractory linings must be used throughout the reactor/regenerator system to avoid erosion due to the catalyst.

In order to ensure that catalyst flows in the desired direction, it is usual to design the unit so that there is a minimum of 0.35 bar positive pressure differential across the catalyst control valves. This is done by choosing the correct regenerator elevation and operating pressure to provide the necessary catalyst driving head.

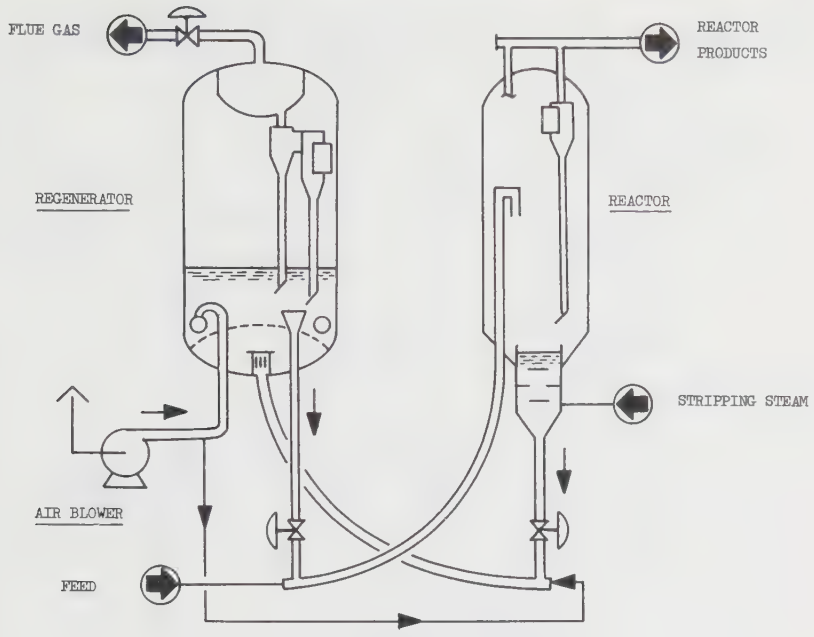


FIG. 9. Model III reactor/regenerator design.

Reactor pressures are normally 1–2.5 bars (g), but in the earliest designs the regenerator was operated at atmospheric pressure. This necessitated mounting it on a very tall structure to obtain the necessary head of pressure above the regenerated catalyst control valve. By operating the regenerator at about 0.55 bar (g), the reactor and regenerator could be mounted at about the same level and the height of structure reduced. This was the 'pressure balance' design shown in Fig. 9, which makes use of high-velocity air to transport the spent catalyst from the reactor to the regenerator.

In later designs, the regenerator pressure was raised to 1.4–2.8 bars (g), which permitted the use of self-supporting vessels with the reactor mounted on top of the regenerator. This also permitted the use of vertical catalyst transfer lines which reduced the erosion caused by the catalyst at high velocities in curved transfer lines. An example of this design is the modern Kellogg Ultra-Orthoflow arrangement shown in Fig. 10. In this design, rapid disengagement of catalyst from reactor products is effected by a cyclone separator mounted directly at the top of the reaction riser.

Early catalytic crackers often suffered from erosion of catalyst control valves, and these were eliminated in the Esso Model IV design (Fig. 11). Both the reactor and regenerator are operated at about 1.5 bars (g), and catalyst transfer is through U-tubes. Spent catalyst in the leg of the U from the stripper is in the dense phase, and by injecting air at the base of the U, the catalyst in the leg rising to the regenerator is maintained in the dilute phase. The difference in density between the two legs gives rise to a pressure differential which causes the catalyst to flow in the desired direction. Catalyst flow from the

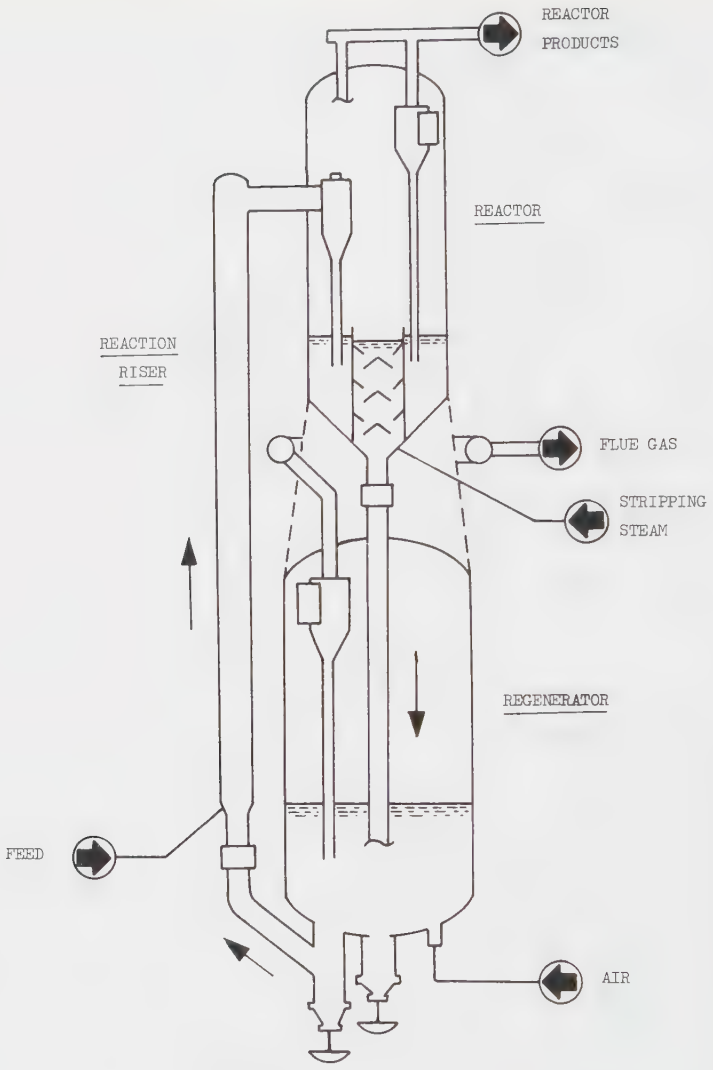


FIG. 10. Kellogg Ultra-Orthoflow catalytic cracker.

regenerator to the reactor is obtained in a similar manner by injecting feedstock and steam into the riser leg to the reactor. The rate of catalyst flow with this design can be controlled by adjusting carrier air rates, or by manipulating regenerator pressure.

Yields and Operating Variables

The catalytic cracking process produces a wide range of products, including gas, C_3/C_4, gasoline and light cycle oil, as well as residual oil and coke. The degree of cracking is traditionally expressed in terms of the '430 Conversion',

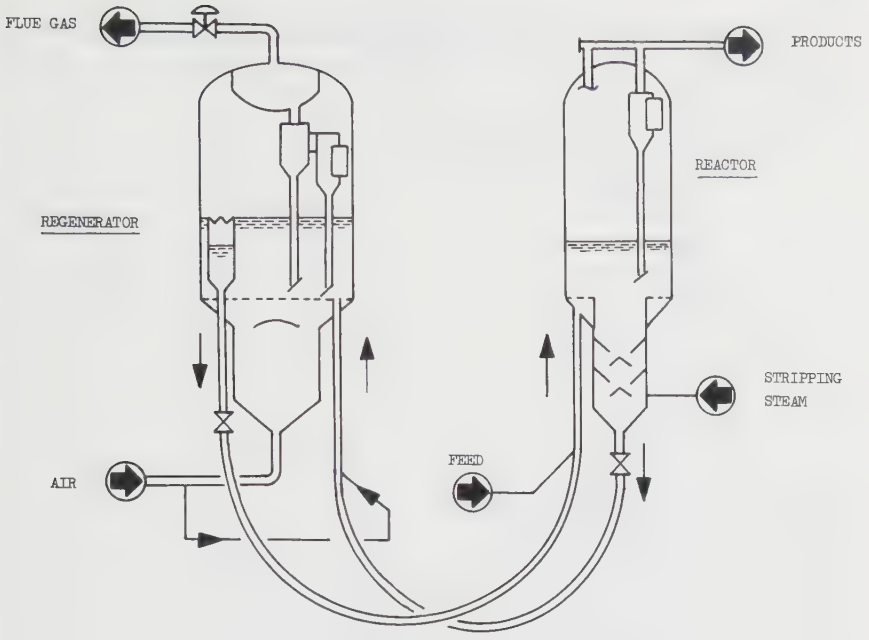


FIG. 11. Essor Model IV catalytic cracker.

which is defined as 100 minus the volume percentage yields of residual oil and light cycle oil boiling above 430°F (221°C). This definition is arguably of little relevance today, however, since the boiling range of catalytic cracker feedstock is typically 350–550°C, and there is obviously a significant yield of product boiling between 221 and 350°C, which can also be considered as 'converted' material. A more realistic and relevant measure of the degree of cracking is given by the total distillate yield, which is defined as the volume percentage yield of products boiling in the range C_5–350°C.

The product distribution obtained from a catalytic cracker depends on a number of operating variables, the most important of which are listed below.

Reactor temperature
Feed preheat temperature
Catalyst circulation rate
Catalyst activity
Recycle rate

Reactor temperature, which is normally within the range 480–540°C, is frequently used to control the degree of conversion. Higher reactor temperatures result in an increase in the yield of the lighter products, and usually a temperature is selected which satisfies finished product demand pattern and is within the design capability of the plant. At reactor temperatures below 525°C, higher temperatures produce more gasoline, but at temperatures beyond 525–535°C, the gasoline itself begins to crack and yield begins to decline. This phenomenon is often referred to as 'over-cracking'.

TABLE XI

	Reactor temperature	
	500°C	525°C
Feedstock		
Density at 15°C	0.917	0.917
Sulphur, % wt	1.80	1.80
Yields		
H_2S, % wt	0.55	0.60
H_2, % wt	0.01	0.02
Methane, % wt	1.1	1.6
Ethane, % wt	1.1	1.4
Ethene, % wt	0.6	0.8
Propane, % vol	2.1	3.2
Propene, % vol	4.9	8.3
Isobutane, % vol	3.8	4.7
n-Butane, % vol	1.5	1.5
Butene, % vol	5.7	7.5
Gasoline C_5–221°C, % vol	51.0	56.7
LCO 221 350°C, % vol	22.3	16.0
Residual oil, % vol	15.2	10.6
Coke, % wt	4.7	5.1
Gasoline octane		
RON–Clear	89.4	92.2

Another important effect of increasing reactor temperature is to give higher gasoline octane numbers. Typical yields for cracking a Middle East feedstock at reactor temperatures of 500 and 525°C are given in Table XI.

Large changes in feed preheat temperatures are not normally possible on a catalytic cracking unit. However, lower preheat temperatures result in an increase in catalyst circulation rate, which directionally increases the yields of lighter products. Coke yield will also increase, at a rate of 0.10–0.15% wt on feed for every 10°C reduction in preheat temperature, but if the plant is limited by regenerator combustion air availability, low preheat temperatures may not be possible.

Substantial changes in yield patterns can be obtained by using catalysts of different activities. Directionally, higher catalyst activities will increase conversion, but too much activity can result in undesirable secondary reactions and over-cracking, depending on the design of the plant. The major step forward on product yields was made when the original low and high alumina amorphous catalysts were replaced by catalysts which contain zeolites. A comparison between low alumina and a modern zeolite catalyst, given in Table XII, shows a considerable increase in conversion to high-value products such as gasoline, with a reduction in the yield of coke.

In older designs, with low activity catalysts, it was common to recycle large quantities of unconverted material back to feed in order to obtain the required level of conversion. The recycle material, generally referred to as heavy cycle oil and boiling in the range 350–450°C, was often recycled at rates up to 100 per cent of the fresh feed rate to the plant. With present-day high activity catalysts,

TABLE XII
Fluid Catalytic Cracking—Yields with Different Catalysts

	Low alumina (recycle operation)	Zeolite (once-through operation)
Gas, % wt	3·9	3·2
Total C_3, % vol	10·5	5·2
Total C_4, % vol	15·4	7·9
Gasoline C_5–210°C, % vol	47·8	58·4
LCO 210–350°C, % vol	24·8	25·0
Residual oil, % vol	9·9	9·5
Coke, % wt	6·6	4·1

sufficient conversion can now be obtained on a once-through operation, and recycle has been largely discontinued.

Apart from the operating variables already described, there are a number of other factors which can also affect the yields obtained on a fluid catalytic cracking unit. Plant design is obviously of great importance. In particular, the hydrocarbon residence time in the reaction zone, as well as the method of mixing the feedstock with the catalyst at the base of the reaction riser, can have a significant effect. The efficiency of catalyst regeneration is also very important. The residual coke on a poorly regenerated catalyst will block off some of the active cracking sites and reduce the effective activity of the catalyst, leading to loss of conversion and gasoline yield. Hence, regenerator design and operation can also have a significant effect on product yields.

Feedstock

The feedstock to a catalytic cracking plant usually consists of a heavy distillate boiling within the range 350–550°C, which is obtained by distillation of reduced crude or atmospheric residue under vacuum. In North America this material is usually referred to as vacuum gas oil, but elsewhere the terms vacuum distillate or 'waxy' distillate are often used. The need for vacuum distillation of cracker feed arises from the requirement to exclude contaminants such as organo-metallic complexes and asphaltenes from the unit. Organo-metallic compounds are a catalyst poison, while asphaltenes increase the yield of coke and may result in unacceptably high regenerator temperatures.

Other feedstocks may include atmospheric gas oils boiling below 350°C, heavy gas oils obtained from thermal cracking operations such as cokers and visbreakers, hydrocracker residues, solvent de-asphalted oils, etc. In some cases, a proportion of reduced crude may also be included in cracker feed, provided that the contaminant levels are not too high.

The way in which a given feedstock will crack depends on a number of factors and, apart from the operating variables already described, the most important of these is the hydrocarbon nature of the feedstock itself. Unfortunately the composition of cracker feedstock is particularly complex, and the range of hydrocarbon types present very diverse. Measurement of the exact hydrocarbon composition is therefore very difficult, if not impossible, by

all but the most sophisticated techniques. Characterization of cracker feedstocks is often carried out by estimating the concentration of aromatic, paraffinic, and naphthenic carbon atoms by relatively simple techniques such as infra-red absorption or using refractive index/density correlations.

In general, the 'crackability' of a feedstock is inversely proportional to the concentration of aromatic carbon atoms (C_A). Aromatics are the most refractory of cracker feed components due to the extreme difficulty with which carbon carbon bond scission occurs within an aromatic nucleus. Aromatics also significantly affect the coke-forming tendency of a feed. Naphthenes are are more reactive than aromatics and crack readily to olefins by ring cleavage. However, there is also a tendency for naphthenes to be transformed into aromatics by hydrogen transfer reactions, which can inhibit conversion. Although less reactive than naphthenes, paraffins are able to crack to a greater degree and therefore tend to give the highest conversion.

The Watson K-factor, determined from a mean average boiling point/specific gravity relationship, is another means adopted for characterizing catalytic cracker feedstocks. Generally, the highly paraffinic feedstocks of $K = 12.0$ give the highest gasoline yields, naphthenic feeds of $K = 11.5$–11.6 give intermediate yields, while the highly aromatic or refractory feedstocks of $K = 11.3$ give very poor yields. A comparison of the yields obtained by catalytically cracking paraffinic North Sea and naphthenic Middle East vacuum distillate feedstocks is presented in Table XIII.

Catalytic cracker feedstocks usually contain a range of contaminants, which can affect operation in a variety of ways. These include: sulphur, nitrogen, and metals.

Depending on operating severity, approximately 30 50 per cent of the sulphur present in feedstock decomposes under catalytic cracking conditions to H_2S. This leaves the plant mainly with the tail gas product and is usually recovered for sulphur manufacture by alkanolamine extraction. The remaining sulphur compounds, which tend to be aromatic in nature (e.g. thiophenes, benzthiophenes), are distributed amongst the liquid product streams and are mainly concentrated in the light cycle oil and residual oil. A

TABLE XIII

Comparison of Yields From North Sea and Middle East Feedstocks

	North Sea	Middle East
Feedstock		
Density at 15°C, g/cc	0.905	0.935
Sulphur, % wt	0.6	3.0
Watson K	12.0	11.7
Yields		
Gas, % wt	6.8	7.0
Total C_3, % vol	10.4	9.6
Total C_4, % vol	13.6	12.6
Gasoline C_5–210°C,	59.4	55.3
LCO 210–350°C, % vol	16.6	18.5
Residue, % vol	6.2	9.5
Coke, % wt	4.8	4.9

proportion of the sulphur also leaves the reaction zone with the coke, and is eventually burnt to SO_2 in the regenerator.

Nitrogen compounds are present in catalytic cracker feedstocks at levels ranging from a few hundred to a few thousand ppm N_2. These compounds partially decompose to NH_3 and HCN, but otherwise leave the unit with the coke and liquid products. Where the nitrogen is present as a basic compound, temporary catalyst de-activation and loss of conversion can result.

Certain heavy metals, notably nickel and vanadium, can be present in catalytic cracker feedstocks as naturally occurring organo-metallic complexes. These compounds completely decompose under catalytic cracking conditions and the metals are deposited quantitatively on the surface of the catalyst. Both metals are serious catalyst poisons, and their effects will be discussed under Catalyst Activity Maintenance.

Hydrotreatment of catalytic cracker feedstocks to remove sulphur is sometimes practised to meet product quality specification requirements, or for environmental reasons to reduce regenerator flue gas SO_2 emissions to atmosphere. Under the conditions normally employed, there is also a substantial reduction in the levels of other contaminants, including nitrogen and heavy metals. Of perhaps greater importance, hydrotreatment of cracker feedstocks can also result in the partial hydrogenation of polynuclear aromatic compounds and therefore can significantly improve their overall crackability. In general, the greater the hydrogen up-take during the hydrogenation step, the higher will be the conversion and gasoline yield and the lower will be the coke yield. Unfortunately, the economics of feedstock hydrotreatment are generally unfavourable, however, due to high installation and operating costs.

Catalyst Activity Maintenance

During the cracking process, the catalyst slowly loses its activity due to the continuous cycling between reactor and regenerator conditions, and it is necessary to add fresh catalyst continuously to maintain conversion at the desired level. The rate at which the catalyst must be replaced, of course, depends on many factors, such as catalyst hydrothermal stability and regenerator temperatures, and typical addition rates may vary between 1 and 2 per cent of catalyst inventory per day. Inevitably, however, some catalyst is lost from the system via the regenerator and reactor cyclones, but often the rate at which catalyst is lost is less than the required addition rate. Under these circumstances, it is necessary to withdraw some of the equilibrium catalyst from the unit every few days in order to maintain the inventory within acceptable limits.

In order to monitor catalyst activity, samples are periodically tested on a small laboratory test apparatus, which determines conversion with standard feedstock and cracking conditions. Catalyst de-activation can occur on the plant for a variety of reasons. Excessive temperatures in the regenerator (735 °C+) can cause hydrothermal de-activation and eventually damage the catalyst structure. This can be particularly severe if steam or emergency spray water is being used to cool the regenerator internals.

Contamination with vanadium or sodium will also cause irreversible loss of activity. These metals are highly mobile within the catalyst structure and

neutralise the active acid sites. At high concentrations they form low melting point eutectics and cause damage to the catalyst pore structure. Nickel is also a serious catalyst poison, but although it has little effect on activity, this metal can promote undesirable dehydrogenation side reactions which may result in a large increase in hydrogen production. Not only can this overload the gas concentration section of the unit, but it may also have an adverse effect on yields.

A recent development by Phillips Petroleum, in which an antimony-containing additive is injected into the cracker feedstock, is claimed to reduce the dehydrogenation activity of nickel substantially. It is believed that antimony effectively 'passivates' the nickel by forming an antimony–nickel complex on the catalyst surface.

Unit Control and Heat Balance

A typical control system for the reactor/regenerator is shown diagrammatically in Fig. 12. Fresh feed and recycle enter the base of the reaction riser at a controlled flow rate and temperature, and reactor temperature is controlled by the regenerated catalyst to the base of the riser. The catalyst bed level in the reactor (or catalyst stripper) is held constant by the spent catalyst slide valve B, which regulates the flow of catalyst back to the regenerator. Reactor pressure is ultimately regulated by control of the wet gas compressor in the gas concentration system, and regenerator pressure is controlled by a differential

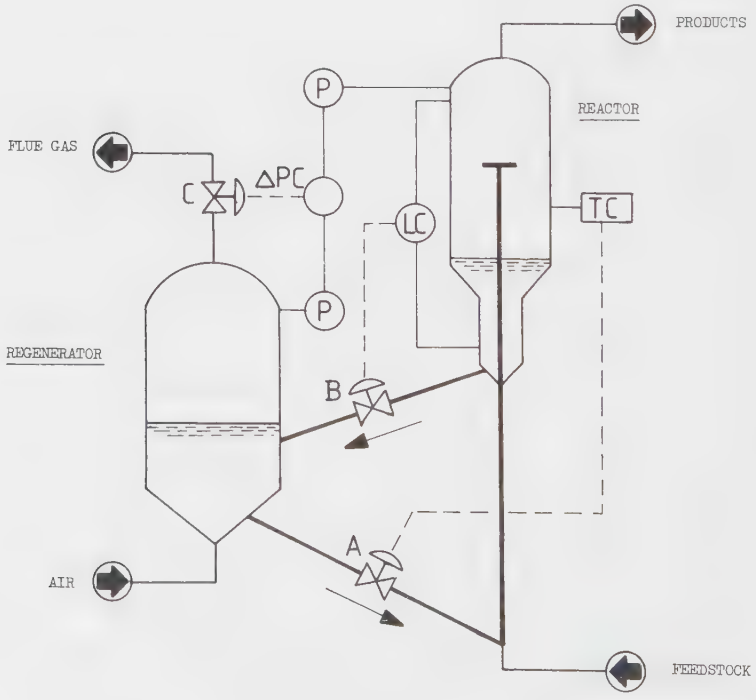


Fig. 12. Typical reactor/regenerator control system.

pressure instrument between reactor and regenerator acting on the flue gas slide valve C.

The catalytic cracking process as a whole is endothermic. Heat is required by the reactor system, not only to satisfy the endothermic heat of the reaction, but also to heat the feedstock from preheat to reactor conditions and to supply the latent heat of vaporization. This heat is provided entirely by combustion of the coke in the regenerator, and hence the coke product can be considered to be the fuel for the process. Most of the heat produced by burning the coke in the regenerator is transferred to the reactor system by means of the circulating catalyst, the flow rate of which is regulated by slide valve A. The reactor/regenerator heat balance is self-compensating over a wide range of operating variables, so that only sufficient coke will be produced to satisfy the total heat demands of the process.

Contrary to an earlier held belief, the coke yield from the catalytic cracking process is not necessarily a function of conversion, but is largely the result of the reactor/regenerator heat demands. Only a minor proportion of the coke is in fact formed by catalytic cracking reactions. Most of the coke is produced as a result of physical adsorption on the catalyst surface of polynuclear aromatics, which subsequently condense under the influence of temperature and residence time to form hydrocarbon material which is no longer volatile at reactor conditions. Since most of the polynuclear aromatics taking part in these condensation reactions originate from the feedstock, the non-volatile coke which forms cannot therefore be the consequence of conversion of feed to lighter hydrocarbons.

For a given feedstock and catalyst type, the coke yield is dependent upon the rate of catalyst circulation through the reaction zone, regardless of whether a change in circulation rate results in any change in conversion. Thus, an increase in catalyst circulation will result in a higher coke yield, while a decrease in circulation rate will reduce coke yield. Referring again to Fig. 12, it follows that any factor that increases the heat demand of the reactor will increase the catalyst circulation rate, and coke yield will increase as a result to maintain the system in stable thermal equilibrium. For example, a reduction in feed preheat temperature will initially cause the reactor temperature to fall. The temperature controller will sense this and increase the flow of regenerated catalyst by means of slide valve A until reactor temperature is once more regained. Coke yield will increase as a result of the higher catalyst circulation rate until the additional heat produced in the regenerator exactly balances the increased heat requirements of the process.

The interrelationship between many of the catalytic cracking operating variables can be determined by a study of the reactor/regenerator heat balance. Considering the reactor and regenerator separately, and neglecting some minor items, the heat balance can be expressed by the following generalized equations:

Regenerator:

Heat of combustion of coke = net heat transfer to reactor + heat required to:

(1) raise air to regenerator temperature
(2) raise coke on catalyst from reactor to regenerator temperature
(3) make up convection and radiation heat losses
(4) make up heat removed by catalyst coolers, spray water injection, etc.

Regenerator:

Net heat transfer from regenerator = heat required to:

5) heat feed plus recycle from preheat to reactor temperature
6) vaporize feed plus recycle
7) supply endothermic heat of reaction
8) raise stripping steam to reactor temperature
9) make up convection and radiation heat losses.

By combining these two equations it can be seen that the heat of combustion of coke is equal to the sum of the items (1)-(9). The contribution of each item towards the total heat balance will of course depend on the design of the unit and the operating conditions, but a typical distribution for a modern catalytic cracker operating under the conditions listed in Table XIV would be as follows:

Heating and vaporizing feed (5) + (6)	53% of heat of combustion of coke
Heating air (1)	24% of heat of combustion of coke
Heat of reaction (7)	20% of heat of combustion of coke
Heat losses (3) + (9)	2% of heat of combustion of coke
Other (2) + (4) + (8)	1% of heat of combustion of coke

In general, a reduction in feed preheat temperature or an increase in reactor temperature, will result in increases in catalyst circulation rate and coke yield. Moreover, the recycle of heavy cycle oil or slurry back to feed will have a similar effect, since this will also increase the heat requirements of the reactor. In all cases, an increase in catalyst circulation rate will tend to increase conversion to lighter products, although reactor temperature has a far greater effect on yields than either preheat or recycle.

Regeneration

In the regenerator, the coke formed during the reaction is removed from the catalyst by combustion. Efficient catalyst regeneration is very important since

TABLE XIV
Modern Catalytic Cracker Operating Conditions

Temperatures, °C	
Reactor	518
Feed preheat	232
Regenerator	710
Flue gas	732
Pressures, bars (g)	
Reactor	2.3
Regenerator	2.1
Catalyst: feed ratio, w/w	6.6
Coke yield, % wt	4.85
Heat of combustion, kcal/kg	9 500
Heat of reaction, kcal/kg	93
430 Conversion, % vol	75

residual coke on regenerated catalyst can adversely affect yields by blocking off the active sites and reducing the effective catalytic activity. This is particularly the case with zeolite catalysts when used in modern short contact time riser reactors, since these require less than 0.2–0.3% wt carbon on regenerated catalyst to perform satisfactorily.

The coke produced by the catalytic cracking process consists of a condensed, highly aromatic hydrocarbon containing traces of sulphur and nitrogen compounds at levels dependent on feedstock composition. On combustion in the regenerator this is burnt to form CO_2, CO, water vapour, SO_2, and oxides of nitrogen. With modern regenerator designs it is possible to burn most of the CO completely to CO_2.

Many regenerator designs have been developed over the years and most of these are based on the back-mixed bubbling fluidized bed principle illustrated in Fig. 13. With all designs good air distribution is essential for uniform fluidization and efficient coke removal. Spent catalyst, which may enter the regenerator either below the air distributor or directly into the fluidized bed, must also be well distributed, otherwise non-uniform regeneration may occur. After an average residence time of 10–15 minutes, regenerated catalyst is withdrawn from the fluidized bed via a conical hopper and returned to the reaction system.

Until about 1974, all regenerators operated with only partial combustion of carbon to CO_2. At regenerator conditions of 620–675 °C and low excess oxygen

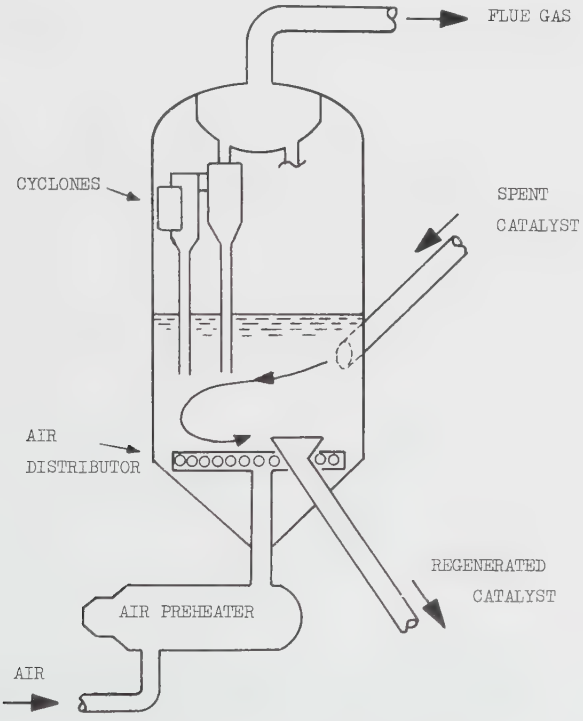


Fig. 13. Back-mixed fluidized bed regenerator.

levels of 0.1–0.2% vol, the CO_2/CO ratio in the flue gas would typically have been 0.8–1.3 vol/vol. One of the problems often encountered with this operation was 'after-burning', which is the combustion of CO with excess oxygen in the dilute phase above the fluid bed. The additional heat release could cause excessive flue gas temperatures and overheat the cyclones to the point of metallurgical failure, if not controlled.

The risk of after-burning can be minimized by carefully controlling combustion air rates to maintain excess oxygen at low levels. Uniform air distribution is also of great importance to avoid large gas bubbles by-passing the fluid bed. Another method of control is to inject spray water to reduce cyclone temperatures, but this has a deleterious effect on catalyst activity as steam quickly de-activates the catalyst at high temperature. The use of spray water is therefore normally reserved for emergencies to contain uncontrolled temperature run-aways.

The most important advance in catalyst regeneration has been the development of systems which enable the complete combustion of CO to CO_2. This has resulted in a significant decrease in the residual carbon content of regenerated catalyst and, whereas 0.3–0.4% wt was typical of previous operations, carbon levels as low as 0.05% wt can now be achieved. Moreover, complete combustion of CO in the regenerator has increased the heat of combustion from approximately 6700 kcal/kg for a CO_2/CO ratio of 1.0 to typical values of about 9300 kcal/kg, and consequently less coke is now required to satisfy the heat demands of the process. In practice, complete CO combustion has resulted in reductions in coke yield of 20–30 per cent, and in many cases this has been accompanied by an increase in conversion due to the cleaner and therefore more active regenerated catalyst.

To withstand the higher temperatures arising from complete CO combustion (680–760°C) changes in regenerator metallurgy have been necessary, and 18/8 stainless steel is now extensively used. The higher velocities employed in modern regenerators to improve air/catalyst mixing help to minimize uncontrolled after-burning. This has been ascribed to the presence in the dilute phase above the fluid bed of more catalyst which acts as a heat sink by removing excess heat from the flue gas.

A totally novel approach to complete CO combustion has been developed by Universal Oil Products in their 'high efficiency' regenerator design shown in Fig. 14. Spent catalyst from the reactor enters the lower regenerator vessel or 'combustor', where the coke is burnt off under conditions of fast fluidization. The contents of the lower regenerator are then transported at high velocity via the combustion riser into the upper regenerator vessel where disengagement of regenerated catalyst from the gas takes place. Regenerated catalyst collects in the annular zone in the base of the upper regenerator from where it is returned to the reaction system in the normal way. In order to maintain temperatures in the combustor high enough to burn the CO within the time available, hot catalyst from the regenerator is recycled to the combustor via the recirculation line.

Nowadays, it is common to minimize, or even eliminate after-burning by dosing the catalyst inventory with minute amounts of an oxidation promoter. This consists of a noble metal such as a platinum finely dispersed on the catalyst surface, which greatly enhances the rate of CO oxidation to CO_2 so that

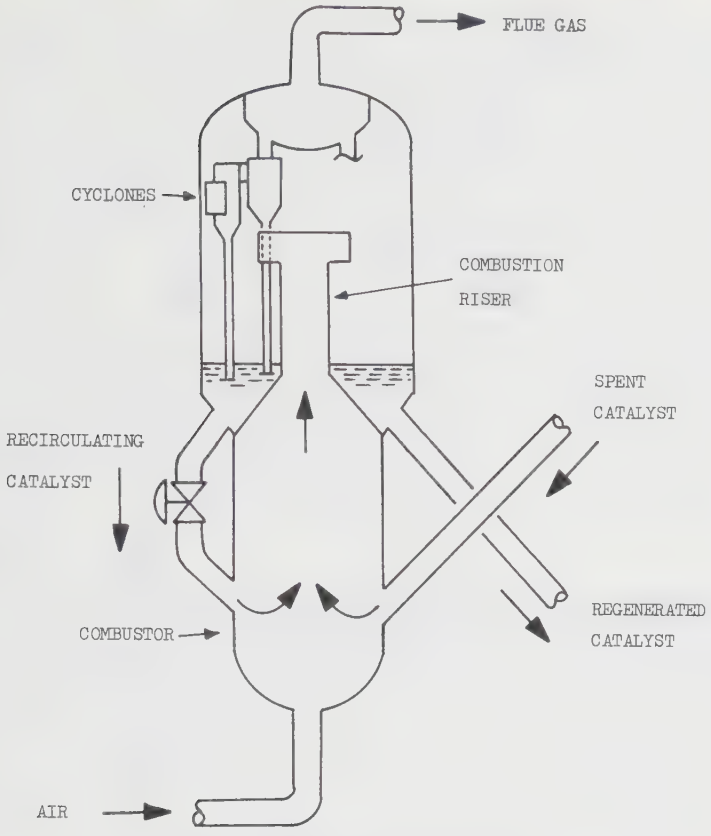


FIG. 14. UOP high efficiency regenerator.

combustion can be confined to the fluid bed. The most important benefit of the promoted operation is that it allows unrestricted combustion of CO in the regenerator without the risk of uncontrolled after-burning.

The air requirements for burning coke depend on a number of factors, including CO_2/CO ratio and the hydrogen content of the coke. For operations with a CO_2/CO ratio of 1.0, the regenerator air consumption would typically be 10.3 kg per kg at coke burnt with coke containing 6.5% wt hydrogen. With complete CO combustion, the air requirements increase to about 13.4 kg per kg coke at 1.0% vol excess oxygen, but the lower coke yield with complete CO combustion can often mean that the overall air requirement of the processes is in fact lower.

Flue Gas Energy Recovery

The high energy content of the high temperature flue gas leaving the catalytic cracker regenerator usually justifies the installation of an energy recovery system. The simplest system used is a waste-heat boiler which recovers the sensible heat from the flue gas by generating high pressure steam. In cases

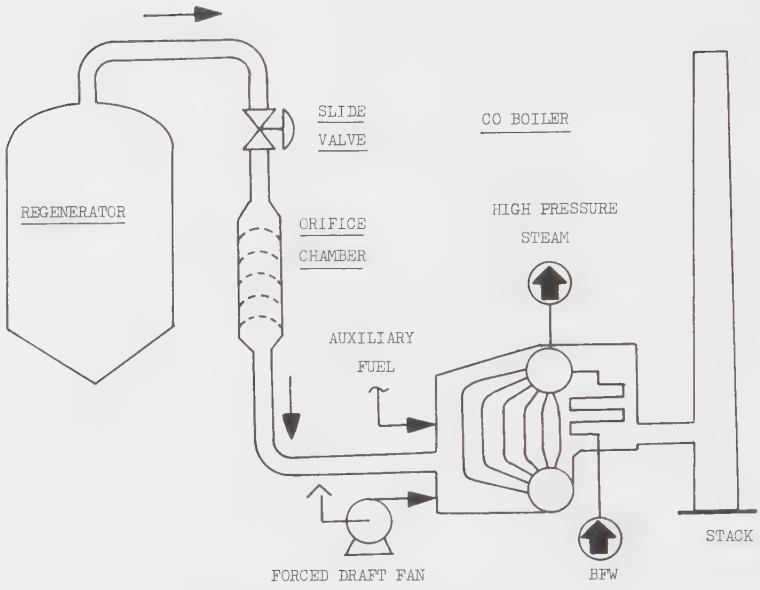


FIG. 15. Flue gas energy recovery with CO boiler.

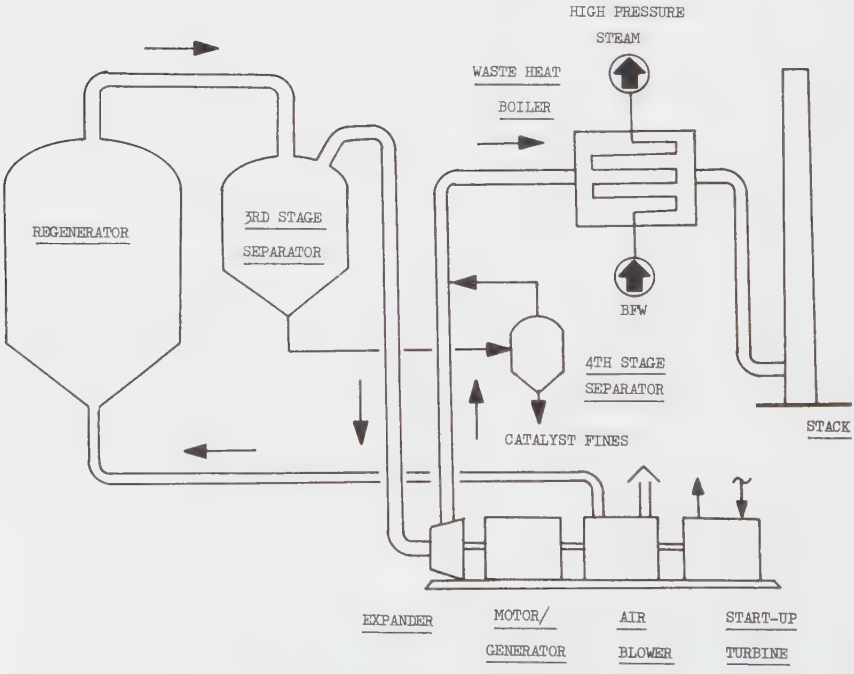


FIG. 16. Flue gas power recovery system.

where the regenerator operates with incomplete combustion of CO, the flue gases can be sent to a CO boiler, which not only recovers the sensible heat, but also the heat of combustion of the remaining CO. Not only does the CO boiler recover energy in the form of high pressure steam, but it also eliminates potential atmospheric pollution. A flow scheme for a typical energy recovery system with a CO boiler is shown in Fig. 15.

Where regenerators are operated at pressures greater than 1.5 bars (g), power recovery expansion turbines can be utilized to recover the energy required to drive the air blower. A simplified flow scheme for such a system is illustrated in Fig. 16. To prevent erosion of the turbine blades catalyst must first be removed from the flue gas in an external cyclone separator. An electric motor/generator is provided for air blower start-up purposes (motoring mode) and as a means of exporting any power that is surplus to air blower requirements (generating mode). The decrease in flue gas temperature across the turbine is about 170°C, depending on efficiency, and it is therefore still possible to produce useful quantities of high pressure steam in the downstream waste-heat boiler. Flue gas finally exits via the stack at about 200–250°C.

Product Recovery

Product vapours leaving the reactor at temperatures between 480 and 540°C are sent to the main fractionator (Fig. 17). This column serves the dual purpose of cooling and condensing the incoming vapours, and separating the products. Gasoline and lighter products pass overhead to the gas concentration section, and light cycle oil is taken as a distillate side-draw. Numerous pump-around streams remove surplus heat which is subsequently utilized for reboiling

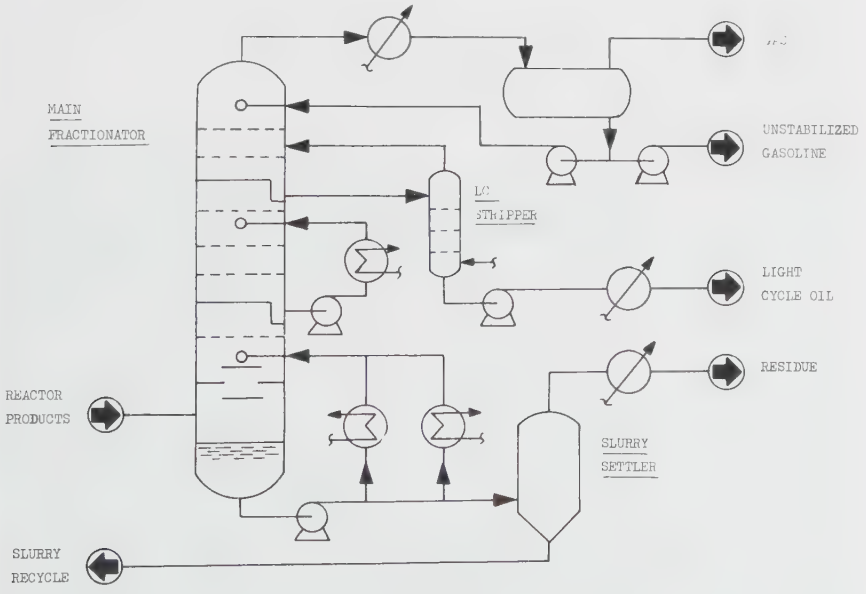


Fig. 17. Catalytic cracker main fractionator.

downstream fractionators. The fractionator bottoms product, which inevitably contains catalyst fines, is sent to a slurry settler to concentrate the catalyst in a slurry stream which is then recycled back to reactor feed.

Overheads gas from the main fractionator is sent to the wet gas compressor which increases pressure to about 12 bars (g). Gas and overheads liquid are then sent to an absorber-stripper system which efficiently separates the C_2 and lighter gases from the remaining products (Fig. 18). The C_3, C_4, and gasoline products are subsequently separated by conventional fractionation.

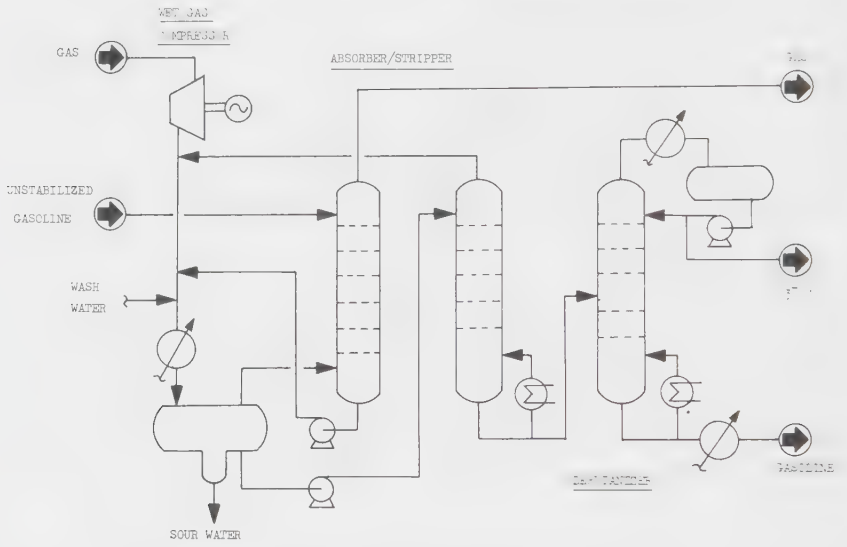


FIG. 18. Gas concentration system.

Product Quality

C_3–C_4. The C_3–C_4 LPG product, as produced from the catalytic cracker debutanizer, contains hydrogen sulphide and mercaptan impurities. These are generally removed from the combined C_3 C_4 stream by alkanolamine and caustic soda extraction prior to separation on the C_3–C_4 splitter. The final C_3 product contains about 70 per cent propene, and can either be used as chemical plant feedstock or upgraded into motor gasoline by alkylation or catalytic polymerization. The C_4 product, which contains about 50 per cent butene and 35 per cent isobutane, can be blended directly into motor gasoline or upgraded by alkylation or catalytic polymerization:

Gasoline. Before catalytic cracker gasoline can be used in the final motor spirit blend, malodorous mercaptan sulphur compounds must be 'sweetened' by means of processes such as UOP Merox Treatment. This, however, does not result in a reduction in sulphur content and, for a gasoline derived from a Middle East feedstock, this can be as high as 0.23% wt. Typical inspection data for gasoline derived from a mixed North Sea/Middle East vacuum distillate feedstock using a high activity zeolite catalyst are provided in Table XV.

TABLE XV
Properties of Catalytic Cracker Gasoline

Density of 15°C	0.745
Distillation, °C	
IBP	39
10%	56
50%	102
90%	180
FBP	205
Total sulphur, % wt	0.15
Reid vapour pressure, bar	0.5
Aromatic, % vol	22
Olefins, % vol	36
Research octane (unleaded)	91.7
Motor octane (unleaded)	80.8

In common with other olefinic gasolines, this material is characterized by a rather high research octane number, but a low motor octane number. Octane numbers can be improved by operating at high reactor temperatures, and by selecting a catalyst with low hydrogen transfer activity to minimize olefin saturation. In general, catalysts incorporating zeolites in the hydrogen form give higher octane number gasolines than rare earth exchanged zeolites, although there may be a small yield penalty.

Light cycle oil. Light cycle oil produced in a modern, high severity catalytic cracking operation is characterized by a very high aromatic content (mainly two-ring naphthalene derivatives), and this is reflected by its high density, which is typically within the range 0.94–0.98 g/cc at 15°C. Generally, the low cetane index of 15–25 makes this material a poor quality diesel fuel blending component, and it is therefore often used as a diluent in heavy fuel oil blends. Sulphur contents are typically 1.1–1.5 times greater than in catalytic cracker feedstock, so catalytic hydrodesulphurization is often carried out, depending on finished product requirements. This material can also be upgraded into gasoline by hydrocracking.

Residual oil. In common with light cycle oil, the residual oil from the catalytic cracking process is high in aromatics content and density (1.05–1.10 g/cc at 15°C). This material is usually blended directly into fuel oil, or alternatively can be used as a feedstock in carbon black or needle coke manufacture.

HYDROCRACKING

High pressure hydrogenation has been used in the refining of petroleum for over fifty years, the first commercial process coming on stream in 1927. This plant used lignite as feedstock and operated at pressures of about 200 bars (g). The main product was gasoline.

As crude oil production increased and new processes such as catalytic cracking were developed, the hydrogenation route for gasoline production became uneconomic and was little used after the early 1940s.

Interest in hydrogenation processes was rekindled in the mid-1950s in the

United States, where market demand required the production of large yields of high-quality motor gasoline at the expense of fuel oil. A contributory factor was the extensive installation of catalytic reforming capacity with its production of large quantities of hydrogen as a by-product.

Since then, a large number of hydrocracking units have been built to convert gas oils and waxy distillates to naphtha and kerosine. The rapid increase in capacity has resulted because of two main factors. First, the versatility and flexibility of the process can give a variety of products in high yields and, secondly, the development of more active and selective catalysts has permitted operation at economically more attractive operating conditions. A further bonus, in a more environment conscious age, is that the products have very low sulphur and nitrogen contents, thereby producing less sulphur and nitrogen oxides when they are subsequently burnt.

Hydrocracking Reactions

Hydrocracking is used primarily to produce low boiling fractions from feedstocks such as heavy gas oils and waxy distillates, and is being extended to residues. The heavier feedstocks contain many polycyclic aromatics, and one of the most important reactions is the partial hydrogenation of these compounds followed by rapid splitting of the saturated rings to form substituted monocyclic hydrocarbons. The side chains resulting from these reactions can be readily removed from the remaining ring structure to yield isoparaffins. Isomerization of the low boiling paraffins is slow under hydrocracking conditions, so iso/normal paraffin ratios are much higher than one would predict on the basis of thermodynamic equilibria.

Paraffin cracking also occurs and the reaction path is similar to that of catalytic cracking. Carbonium ions are produced via olefin intermediates. The carbonium ions then crack and the fragments are quickly hydrogenated under the high hydrogen partial pressures employed in the process.

This rapid hydrogenation prevents the adsorption of olefinic molecules on to the catalyst surface and their subsequent dehydrogenation to coke as in catalytic cracking. Hence, long on-stream times can be obtained without the need for catalyst regeneration.

The degree of cracking is also dependent on the feedstock. Decalin, which is a multi-ring naphthene, cracks more readily than the corresponding normal paraffin and gives higher iso/normal ratios than obtained from the paraffin. A large yield of single-ring naphthenes is also produced, and these are resistant to further hydrocracking and contain a higher than equilibrium ratio of methylcyclopentane to cyclohexane.

The sequence of hydrogenation and cracking reactions whilst hydrocracking light catalytic cycle oil has been studied, and the rate constants of the various reactions determined. The results obtained are summarized in Fig. 19 and show that:

(a) Polycyclic aromatic compounds are partially hydrogenated rapidly.
(b) Naphthene rings in polycyclic compounds are readily removed by ring opening followed by cracking.
(c) Single-ring naphthenes and paraffins are more resistant to cracking.
(d) Single-ring aromatics are difficult to hydrogenate.

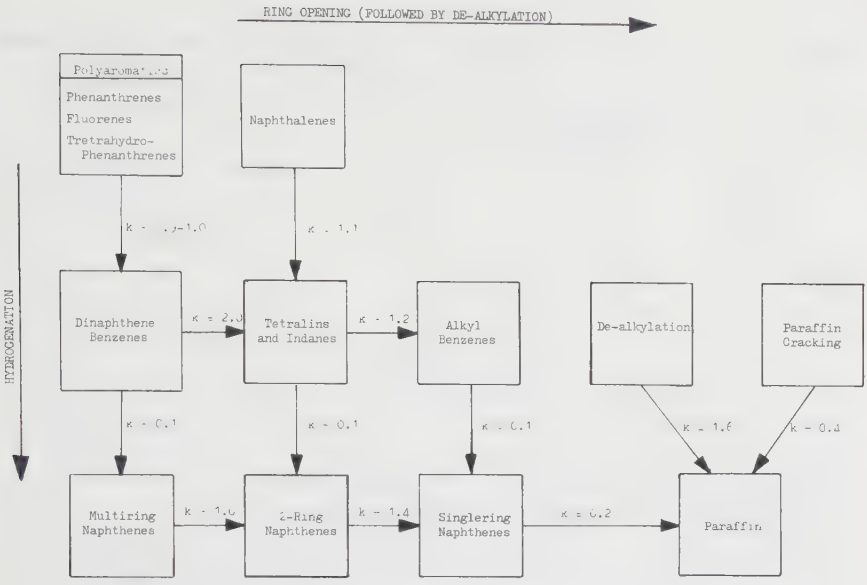


FIG. 19. Relative reaction rate constants in isothermal hydrocracking of light cycle oil at 103 bars.

It was further found that saturated compounds, particularly the paraffins and single-ring naphthenes, appear to react more slowly at lower feed conversion levels that at higher conversion levels. This is believed to be due to the displacement of saturates from the catalyst by the strong adsorption of heavy aromatics initially present in the feedstock.

Catalysts

The hydrocracking reaction, which combines both cracking and hydrogenation reactions, demands a dual-function catalyst. Cracking reactions are promoted by acid sites and hydrogenation by metal sites. The acid function is normally supplied by the catalyst bases and these are primarily amorphous silica-alumina or zeolites. The hydrogenation function is supplied by metals selected from Group VI and Group VIII of the Periodic Table. Favoured metals are molybdenum and tungsten, and cobalt, nickel, platinum and palladium, respectively. The selected metals are dispersed on the catalyst base.

The preferred catalyst base depends on the type of product required. Silica-aluminas are normally used where waxy distillates (350–550°C boiling range) are hydrocracked to maximize the yield of middle distillates (kerosine and diesel oil), whilst zeolite catalysts, which have a higher intrinsic acid activity, are more favoured where the main product requirements are gasoline and naphtha. Zeolite bases are now being developed which enable them to be used satisfactorily for middle distillate production.

These highly acidic catalysts are sensitive to nitrogen compounds in the feedstock. The effect of feedstock nitrogen using a silica-alumina based catalyst under standard processing conditions is shown in Table XVI.

TABLE XVI

Effect of Feedstock Nitrogen on Start-of-Run Temperature and Catalyst Ageing Rate

	350–550°C Feedstock			
Crude Type	Nitrogen Content (ppm)	Sulphur Content (% wt)	SOR Temperature (°C)	Catalyst ageing rate (°C/day)
Kuwait	640	2.50	Base	0.05
IMEG 'A'	765	2.33	Base + 6	0.06
Iran Light	1165	1.72	Base + 14	0.14

The results show that the higher nitrogen content feedstock ages the catalyst almost three times as rapidly, and moreover the average start-of-run catalyst temperature required is much higher. The reason for this higher temperature requirement is believed to be that the ammonia formed in the reaction partially neutralizes the acid sites, thus reducing the catalytic activity.

Zeolite catalysts, on the other hand, are poisoned by organic nitrogen compounds which adsorb strongly on the catalyst. Processes which use a zeolite catalyst require the feed to be pretreated to remove nitrogen to a low level. An example of the effect of nitrogen on the reaction temperature required to maintain a constant catalyst activity level is shown in Fig. 20. Zeolites are sensitive to ammonia, but due to the large number of acid sites available, they still remain very active.

Processes using silica-alumina catalysts may require feedstock pretreatment if the feed nitrogen content is very high. Denitrogenation is usually carried out using a cobalt/molybdenum or nickel/molybdenum-on-alumina or silica-alumina catalyst.

Processes

A number of hydrocracking processes are available for license, the most widely used being Unicracking (Union Oil of California), Isocracking (Chevron Research), and HDC Unibon (UOP). These are fixed bed processes, employing one or two reaction stages dependent on unit size, severity of operation, or product distribution required. Other processes of this type are offered by BP and IFP. Shell also has a hydrocracking process, but it is not normally offered for license. These processes are primarily for converting heavy gas oil and waxy distillate feedstocks.

Three processes are available for residue hydrocracking, namely the BOC fixed bed process (UOP) and two expanded or ebullating bed processes, H-Oil (Hydrocarbon Research Inc./Texaco) and LC-Fining (Cities Services/Lummus). The latter two processes were originally developed for residue desulphurization and have been adapted for residue hydrocracking. A description of the LC-Fining Process is given in the chapter which deals with hydrodesulphurization.

Hydrocracking units have a number of plant configurations and the range of operating conditions is wide. In the large number of technical articles there is a

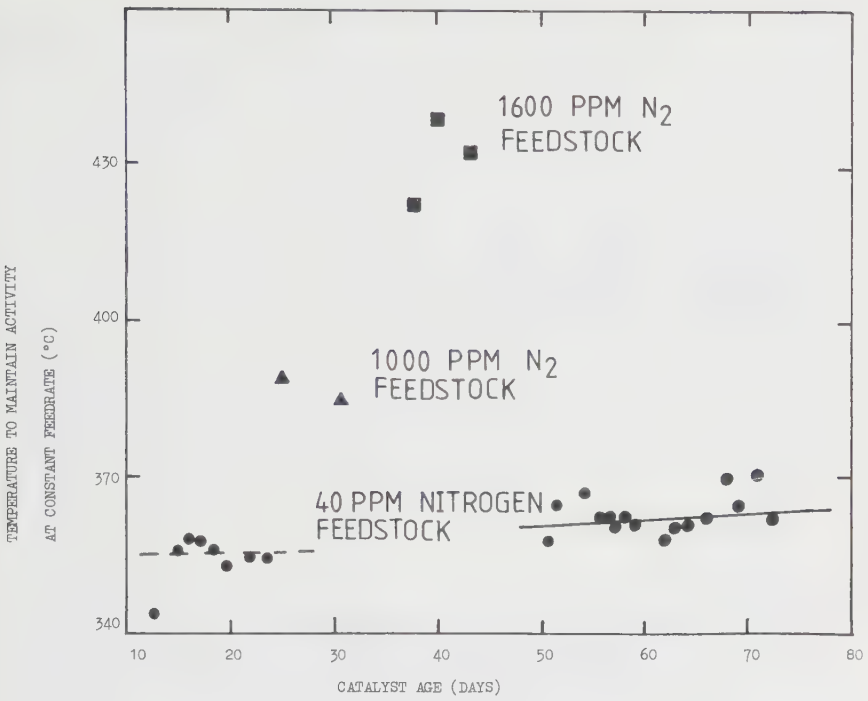


FIG. 20. Effect of nitrogen on catalyst activity at 103 bars.

lack of information on process conditions, but from patents and a small amount of published data it is evident the conditions are severe and range as follows:

Reaction pressure	70–210 bars (g)
Reaction temperatures	300–440 °C
Liquid space velocity	0.3–2.0 v/v/h
Recycle gas rate	800–2000 Nm^3/m^3

The severe conditions are required to obtain a high level of cracking and hydrogenation. As a result of the high pressures used, the hydrogen consumption is high and can vary from 100 to 500 Nm^3/m^3.

Distillate Hydrocracking

Unicracking process

Several processing configurations are available, and by varying process conditions and catalysts within each configuration it is possible to emphasize the production of a variety of products from a wide range of feedstocks.

A single-stage Unicracker is shown in Fig. 21.

Untreated feed and hydrogen-rich make-up gas are charged to the first reactor where hydrotreating reactions convert sulphur, nitrogen, and oxygen compounds to hydrogen sulphide, ammonia, and water, respectively. The effluent from the hydrotreating reactor passes directly to the hydrocracking

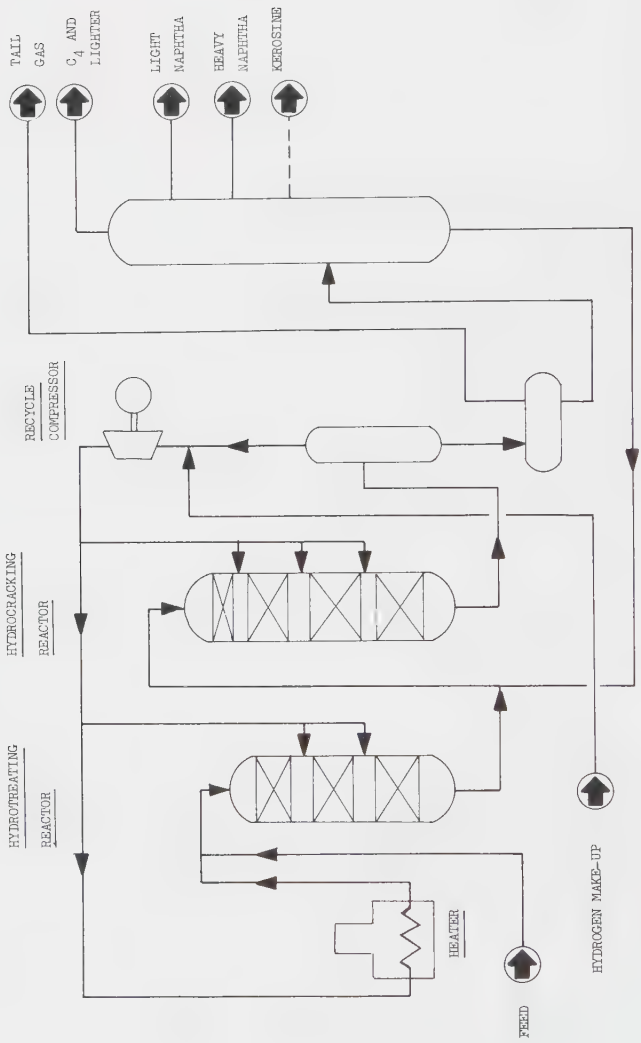


FIG. 21. Single-stage unicracking process.

reactor where 40 to 80 per cent of the reactor charge is converted into lighter products. The effluent is cooled, and the liquid products and unconverted feed are separated from the recycle gas, which is then returned via a recycle gas heater to the reactors. In addition, cold recycle gas is injected between catalyst beds to quench reaction heat and maintain temperature control. The liquid stream is sent to a low pressure separator to remove dissolved gases before product separation in a fractionation tower. Unconverted oil is normally recycled to the cracking reactors and cracked to lower boiling products. Recycle oil (unconverted material) may be withdrawn as a product if required. In larger plants a second reaction stage may be added, and the unconverted oil from the first stage can be converted separately. Union claim that, with improvements in both hydrotreating and hydrocracking catalysts, one particular unit has increased in capacity from 8000 BPSD to 14 000 BPSD over the period of 1963 to 1981. In addition, the catalyst cycle length has been increased from one year to $2\frac{1}{2}$ years.

Typical yields obtained with a non-noble metal catalyst when processing an Iranian wax distillate are shown in Table XVII.

Isocracking process

The Chevron Isocracking Process is also available with a variety of processing schemes and catalysts, depending on the product requirements.

The main difference with the Chevron process is that the feedstock is not normally pretreated to remove nitrogen in a separate reactor. A simplified flow diagram of a single-stage plant is shown in Fig. 22.

In a single-stage isocracker plant the fresh feed is blended with recycle feed and then passed with hydrogen-rich recycle gas through a charge heater to the reactor inlet. The reactants pass over the catalyst in a plurality of beds with inter-bed quench. The effluent from the reactor is then cooled and sent to a high pressure separation vessel. The effluent is separated into liquid products and recycle gas. The gas is recycled to the unit with the addition of hydrogen-rich make-up gas. The liquid products pass to fractionation for separation.

TABLE XVII

Yield Response to Reactor Temperature

Feedstock			
Crude source	Marun (Iranian) 343–540 °C		
Specific gravity	0.9123		
Nitrogen, ppm	1250		
Sulphur, % wt	2.0		
Aniline point, °C	85		
Reactor average temperature, °C	375	367	359
Product	Naphtha	Turbine fuel	Diesel
Yields, % vol			
Butane	19.6	8.9	4.2
C_5–60 °C	21.7	11.3	6.3
60 °C+ naphtha	81.0	45.7	28.5
150 °C+ distillate	—	54.1	75.2
Naphtha endpoint, °C	168	160	163

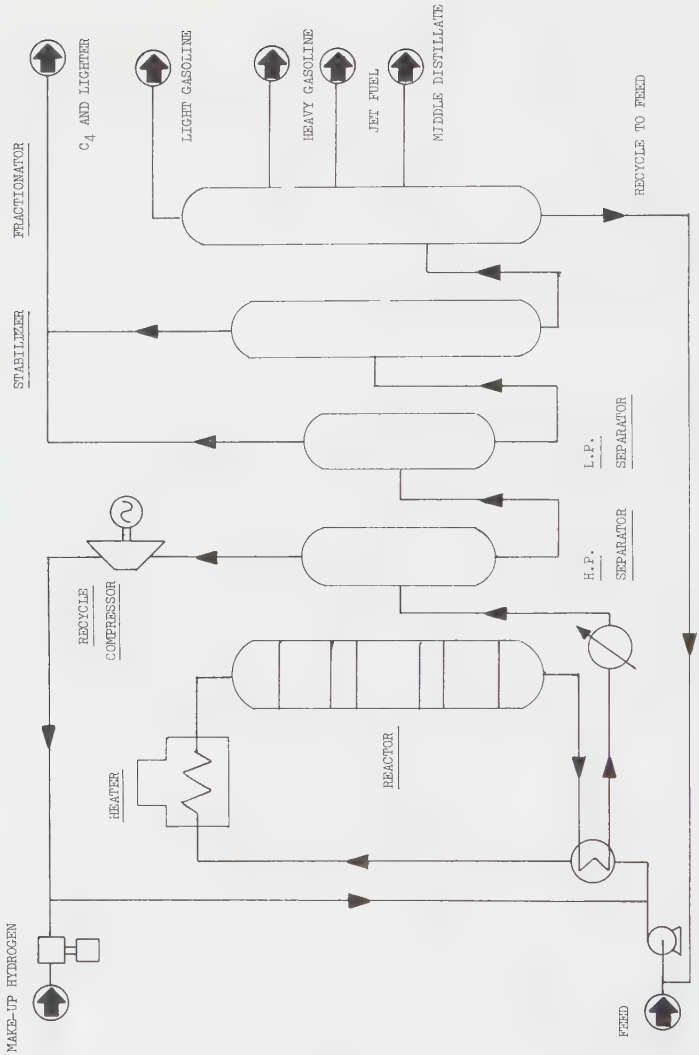


FIG. 22. Chevron single-stage Isocracking Process.

Unconverted feed is taken from the base of the fractionation column and recycled to the process.

In a two-stage plant, each reaction stage has a similar process flow configuration. The first reaction stage removes the nitrogen and hydrogenates the heavier aromatics, converting part of the feedstock to low boiling material. The effluent, after separation, passes to a common fractionator with second-stage effluent. The unconverted material is withdrawn from the base of the column and recycled to the second reaction stage where the remainder of the cracking is carried out.

Typical yield data for commercial two-stage units are shown in Table XVIII.

TABLE XVIII
Isocracking Yield Data

Feedstock	Light cycle oil	Waxy distillates	
Specific gravity, 15/15°C	0.906 5	0.899 6	0.924 2
Boiling range, °C			
10% vol	248	393	393
50% vol	268	454	468
EP	335	565	593
Sulphur content, % wt	0.6	1.0	2.5
Nitrogen content, ppm	500	1 000	900
Aniline point, °C	33	82	82
Product yields, % vol			
Propane	3.4	2.0	—
Isobutane	9.1	1.2	1.2
n-Butane	4.5	1.5	1.4
Light naphtha	30.0	11.9	7.0
Heavy naphtha	78.7	14.2	7.4
Kerosine	—	86.8	50.0
Diesel oil	—	—	51.6

UOP HDC Unibon

The UOP single-stage process is similar in configuration to the Chevron Isocracking Single Stage Unit (Fig. 22). Differences relate to catalyst and processing conditions. Again, the UOP process is available in other process configurations and with various catalysts.

Typical pilot plant process yields maximizing middle distillate product with feedstocks from different crude sources are shown in Table XIX.

Product Properties

The properties of the various products of hydrocracking are very much influenced by the composition of the feed to the process. A basic rule of thumb is 'many rings in, many rings out; few rings in, few rings out'. This is clearly illustrated in Table XX, which shows the naphthene-aromatics (N + A) produced in hydrocracker naphthas as a function of the feedstock UOP Characterization Factor.

TABLE XIX

Pilot Plant Hydrocracking Yields for Maximum Middle Distillate Production

Crude source	Taikei	Libyan	Gach Saran	Agha Jari
Specific gravity, 15/15°C	0.8534	0.8724	0.9117	0.9328
ASTM distillation, °C				
IBP	251	263	269	413
10% vol	313	360	337	449
50% vol	410	433	427	485
90% vol	485	505	516	532
95% vol	506	528	529	543
FBP	—	—	557	—
Total sulphur, % wt	0.04	0.23	1.89	1.96
Total nitrogen, ppm	315	700	1627	1700
Aromatics, % vol	22.7	26.9	48.0	52.7
UOP, K-factor	12.53	12.42	11.82	11.9
Product yield, % wt on feed				
H_2S	0.04	0.25	2.01	2.04
NH_3	0.03	0.09	0.20	0.20
C_1 C_4	3.97	6.53	5.35	7.33
C_5 C_6	6.88	7.93	6.43	7.06
C_7 149°C	16.19	16.69	16.43	17.49
149–266°C	33.22	34.45	35.73	39.40
266 343°C	40.96	35.82	36.40	29.25
Total	101.30	101.76	102.55	102.77

For low UOP K-values (high feed ring content) the total (N + A) production is high and as the value of UOP K increases the quantity of (N + A) produced decreases.

Similarly, the kerosine and diesel oil products reflect the nature of the feedstock as shown in Table XXI. As the feedstock becomes more aromatic the kerosine and diesel oil products become more aromatic as shown by higher gravity for the same boiling range product. The kerosine fraction from a very paraffinic feed has a very high smoke point, and this decreases as the feedstock

TABLE XX

Typical Yields of N + A in 65 C+ Unicracker Naphtha

Fresh feed					(N + A) vol % on Feed		
UOP K	50% PT (°C)	Naphtha end point (°C)	No. of stages	Catalyst	C_6–C_8	C_6–C_9	Total
9.69	247	176	1	NNM	68.8	76.6	83.7
10.20	251	168	1	NM	61.2	71.1	74.4
11.40	352	189	1	NNM	39.7	52.7	60.5
11.79	434	182	2	NNM	29.4	40.9	49.9
11.89	418	178	1	NM	30.8	40.0	44.8
12.45	380	171	2	NM	21.7	27.4	28.5

NM = Noble metal catalyst. NNM = Non-noble metal catalyst.

TABLE XXI
Effect of Feedstock on Distillate Product Properties

Feedstock		Kerosine (149–266°C)		Diesel (266–343°C)	
UOP K	50% Point (°C)	Specific gravity	Smoke point (mm)	Specific gravity	Pour point (°C)
12.53	410	0.7870	35.6	0.8017	−12
12.42	433	0.7949	29	0.8132	−21
11.82	427	0.8128	22.5	0.8241	−21
11.90	485	0.8142	21.9	0.8304	−26

becomes more aromatic. The diesel fraction shows a similar effect with pour point. The product from a paraffinic feedstock exhibits a higher pour point than the product from a more aromatic feedstock.

Reactor Design

The design of the reactors for hydrocracking must be carefully considered due to the severe operating conditions to which they are subjected, namely:

High total pressure
High hydrogen partial pressure
High hydrogen sulphide and ammonia partial pressures
High operating and regeneration temperatures
High exothermic heat of reaction.

Individually these points do not normally cause particular problems, but in combination they require much more consideration.

The high pressures involved and relatively low space velocities mean that the reactor vessels are very large and wall thicknesses can be as much as 250 mm. The high hydrogen partial pressures require special materials of construction, and the presence of high hydrogen sulphide partial pressures requires a stainless steel lining to the vessel. The high operating temperatures require accurate knowledge of the properties of the steels used. This has involved extensive investigations into what would be the effects of variations in composition, grain size, metallurgical structure, and quenching and tempering procedure used upon the creep strength, flow stress and notch ductility of the finished reactor shell.

The heat of reaction is a function of the amount of hydrogen consumed, and is normally in the range 490–630 kcal/m^3 of hydrogen absorbed. For a feedstock absorbing up to 340 m^3/m^3 this represents a heat release of about 220 kcal/kg of feed. To maintain good control of the reaction and to prevent temperature excursions it is necessary to control the reaction temperature accurately and within a narrow range. This is done by splitting the catalyst in the reactor into a number of separate beds with means of cooling the effluent from each bed. This is normally achieved by either:

Injection of cold recycle gas between the catalyst beds, or
Injection of cold recycle liquid between the catalyst beds.

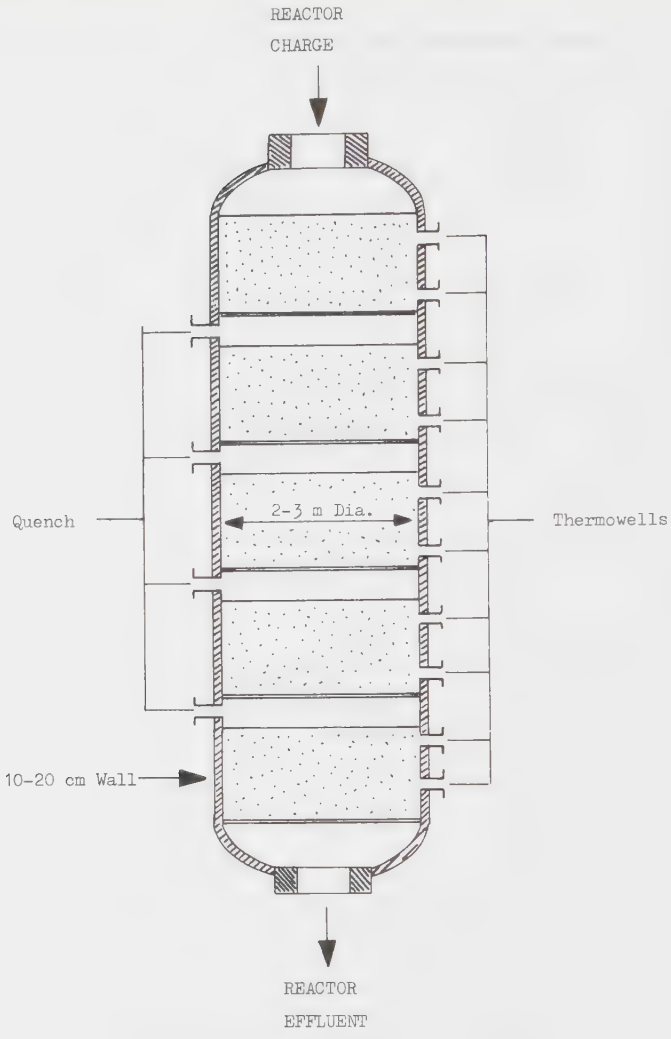


FIG. 23. Typical hydrocracker reactor design.

The first alternative, which cools the product by helping to increase product vaporization in addition to providing an additional heat sink, is the more favoured. Liquid recycle causes difficulty in providing proper liquid distribution within the reactor.

A typical reactor design is shown in Fig. 23 with all the entries for quench gas and thermocouples passing through the side wall of the reactor. To avoid potential mechanical weaknesses and welding problems alternative designs eliminate the nozzle connections in the shell wall and have only two openings in the reactor head for quench gas and thermocouples (Fig. 24). Another design uses concentric vessels, in which the catalyst is contained within a liner which stands on the bottom head manway and supports the vessel internals, catalyst support trays and catalyst. Make-up gas flows up through the annulus between

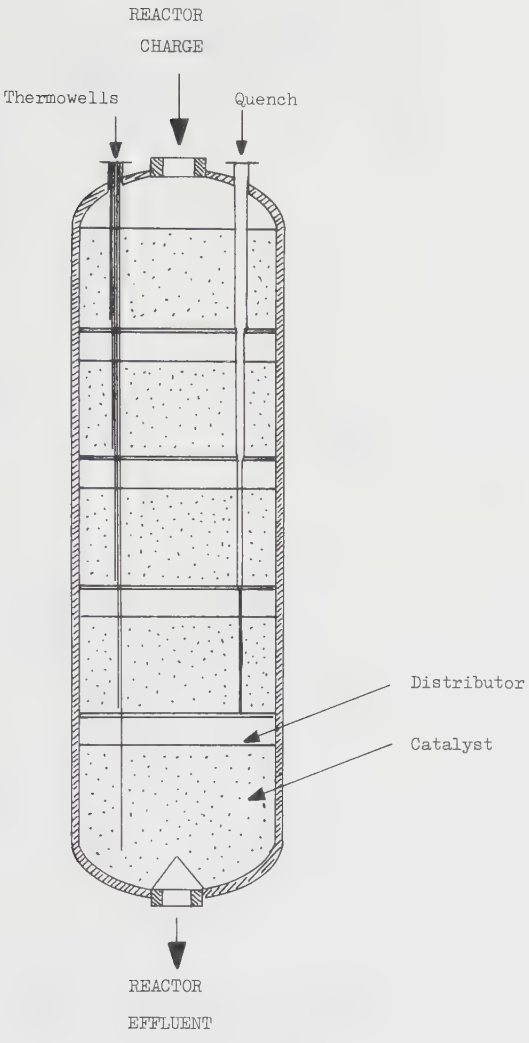


FIG. 24. Alternative hydrocracker reactor design.

the main reactor shell and the liner. This technique prevents contact of corrosive reactor products with the main reactor shell which is maintained at lower than reaction temperature because of the cooling action of the make-up gas. This method of construction also avoids the problems of tray support connections to the main reactor shell.

Residue Hydrocracking

When applied to crude oil residue feedstocks, the hydrocracking process can be used for:

1. Fuel oil desulphurization.
2. Residue conversion to lower boiling distillate.
3. Production of a high-quality synthetic crude oil.

TABLE XXII
Expanded Bed Hydrocracking

Yield structure	345°C+ Residue feedstock	540°C+ Residue feedstock
C_4 and lighter, % wt	10.0	10.5
C_5 205°C, % vol	18.2	18.9
205–345°C, % vol	25.0	25.4
345–540°C, % vol	45.8	35.4
540°C+, % vol	13.1	25.0
C_{5+} liquids, % vol	102.1	104.7
Conversion at 540°C, % vol	75	75
Desulphurization, %	75–90	75–90
Demetallation, %	85–95	85–95
Chemical hydrogen consumption, Nm^3/m^3	170	280

Fuel oil desulphurization has been described under hydrodesulphurization in the next chapter.

As discussed there, one of the problems of processing residues is the deposition of metals, in particular vanadium and nickel, on the catalyst. As it is not possible to remove vanadium from the catalyst, replacement is necessary when the catalyst becomes de-activated. Thus, the time taken to replace the catalyst can significantly reduce the unit time efficiency. The H-Oil process, and more recently, the LC-Fining process were developed to overcome these difficulties. Instead of a conventional downflow fixed bed, the reactors contain the catalyst in the form of an ebullating bed. This enables catalyst to be added and removed from the reactor whilst the unit is on stream. Typical yield data for the hydrocracking mode of operation are given in Table XXII. The gasoline produced is slightly olefinic and requires further treatment before being fed to a catalytic reformer.

A new development in the hydrocracking field is the CANMET process for converting atmospheric and vacuum residue into naphtha and distillates. In this process high conversion and substantial desulphurization are achieved by using a low-cost additive instead of a conventional catalyst.

TABLE XXIII
CANMET Process—Typical Yields

Feed source	Cold Lake	Laguna	Arabian Light
C_4–204°C, % vol	27.0	30.7	28.4
204–343°C, % vol	33.8	36.8	34.8
343–525°C, % vol	36.1	29.6	32.8
525°C+, % vol	5.7	7.4	9.2
Residue conversion, wt %	88	89	87
Desulphurization, wt %	56	60	45
Asphaltene conversion, wt %	72	84	51
Chemical hydrogen consumption, Nm^3/m^3	200	230	210

The feed is mixed with a small proportion of an iron–coal compound, used as a processing additive. The mixture of feed and additive is heated and mixed with hydrogen-containing gas in an upflow reactor. The additive is said to permit high conversion of the feedstock at low pressures by suppressing coking. Conversion is said not to be adversely affected by high levels of feed metals or other contaminants. Typical yields for three vacuum residues are given in Table XXIII.

The first commercial unit of this type is due to be started up at the Petrocanada Refinery in Montreal in 1984.

HYDROGEN PRODUCTION

The hydrogen requirements for hydrocracking units are normally so large that insufficient hydrogen is available from catalytic reforming. In such cases a hydrogen production plant becomes a necessary part of a hydrocracker complex. Two types of process are in common use, steam reforming and partial oxidation.

Steam Reforming

In a typical steam reformer, methane or higher hydrocarbons are reformed with steam at pressures of 15–30 bars (g) and temperatures of 800–870 °C. The basic reactions occurring with methane are:

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

$$CO + H_2O \longrightarrow CO_2 + H_2$$

and with higher hydrocarbons the general equations are:

$$C_nH_m + nH_2O \longrightarrow nCO + \left(n + \frac{m}{2}\right) H_2$$

$$nCO + nH_2O \longrightarrow nCO_2 + nH_2$$

The steam-hydrocarbon reactions are favoured by high temperatures and low pressures. They are also favoured by high steam/carbon ratios. However, as the hydrogen is finally required at high pressure there is an economic incentive to operate the process at as high a pressure as possible. The adverse effects of operating at the higher pressure can be overcome by operating at higher steam/carbon ratios and higher temperatures. This too imposes an economic penalty, and the choice of operating pressure must be made with each particular application in mind. Normally the operating pressure ranges from 15 to 30 bars (g).

In the reaction with higher hydrocarbons methane is also formed, but its equilibrium concentration falls off rapidly with increasing temperature and also with steam/carbon ratio (defined as moles of steam/atoms of carbon). Equilibrium diagrams for the reforming of a C_6 150 °C naphtha are shown in Fig. 25. These clearly illustrate that the higher steam/carbon ratio results in increased hydrogen and lower methane concentrations at the normal steam

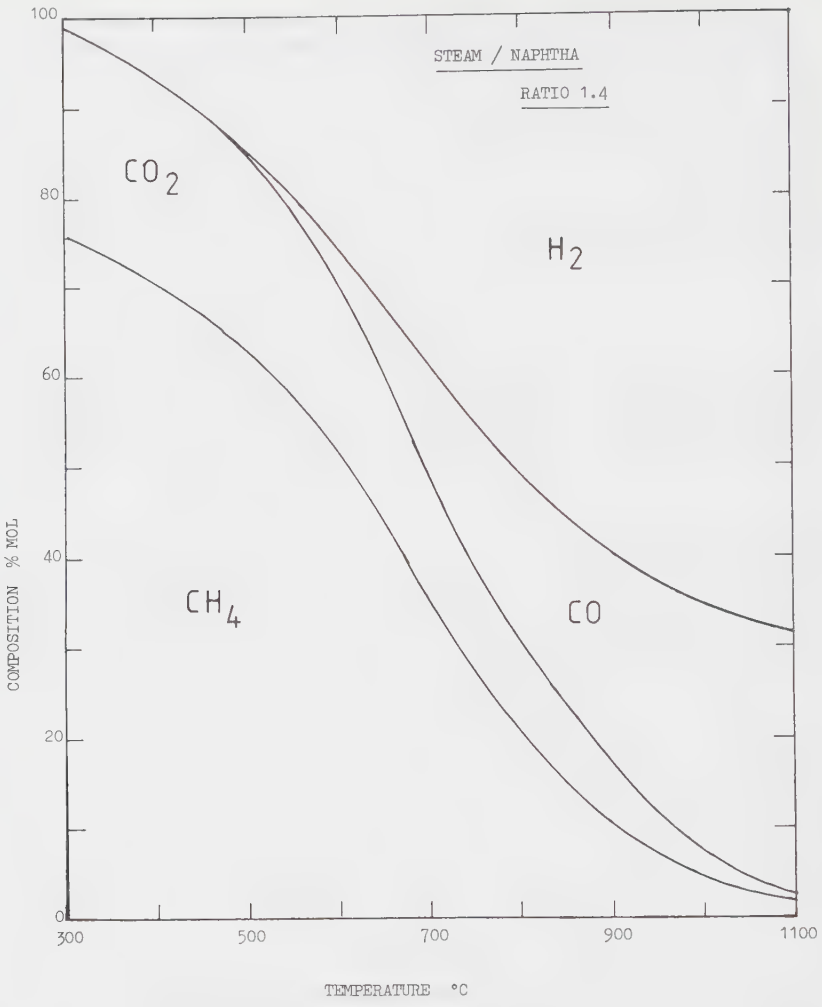


Fig. 25. Equilibrium dry gas compositions: steam/naphtha reforming at 25 bars.

reforming temperatures, 800–870°C. Increased steam also causes more CO to react to give a higher concentration of CO_2.

The product from the steam reforming furnace contains some 25–30 per cent of carbon oxides, which must be removed if high-purity hydrogen is required. The CO can provide hydrogen and CO_2 by passing the reformer effluent over high temperature shift catalyst (water–gas shift reaction). There are two different routes which can be followed to purify the hydrogen.

First, the remaining CO can yield hydrogen and CO_2 by passing the gases over a low temperature shift catalyst. The CO_2 can then be removed by absorption in potassium carbonate or amine solution. The residual amounts of CO and CO_2 can finally be removed by methanation.

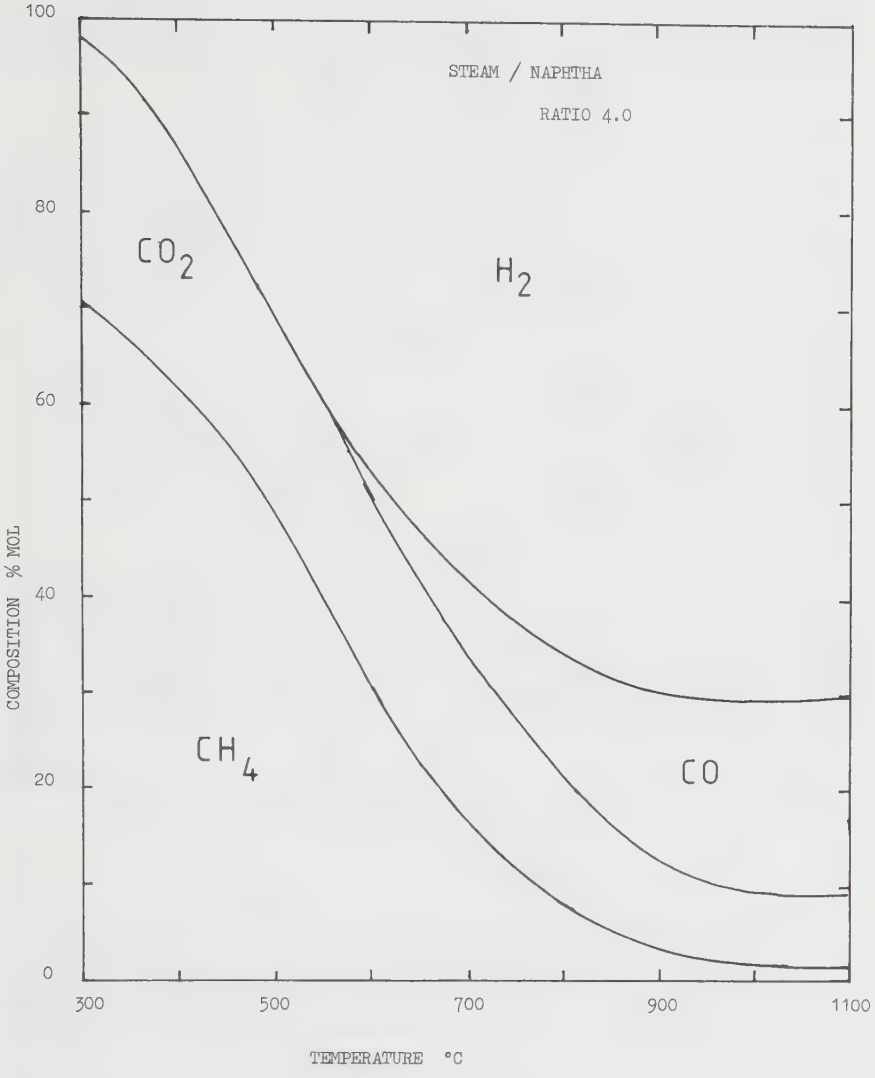


FIG. 25.—*contd.*

Alternatively, the gas is sent to a pressure swing adsorption (PSA) unit, which removes residual CO and all CO_2 and methane along with a small amount of hydrogen. In smaller PSA units using four adsorbers, hydrogen recovery is normally in the range 76 to 78 per cent. For the larger hydrogen plants, a Polybed PSA unit is used. These units have ten adsorbers, and operate with an extra step of pressure equalization, which improves the hydrogen recovery to 84 to 86 per cent.

In the reforming section, the catalyst used is nickel on a refractory alumina base. Some catalysts also incorporate uranium, and more recently lanthanum.

Certain catalysts incorporate an alkaline promoter in the base to help prevent carbon deposition on the catalyst. The catalyst is usually in the form of Raschig rings, 15–18 mm in diameter. Reforming catalysts are very sensitive to sulphur poisoning, and the feed must be desulphurized to less than 1 ppm.

Naphtha feedstocks are desulphurized by conventional treatment with hydrogen over a cobalt–molybdenum alumina catalyst. Gaseous feedstocks with low sulphur contents are satisfactorily desulphurized by passing them over zinc oxide at about 400°C. Occasionally a zinc oxide/cobalt–molybdenum alumina/zinc oxide (purple sandwich) is used. The zinc oxide is replaced when it no longer absorbs sulphur.

The reforming reaction is highly endothermic (54 260 kcal/kg mol for the methane reaction), and to supply this large quantity of heat, the reaction is carried out in a large number of tubular reactors which are normally 100 - 125 mm in diameter and 7.5 to 10.5 m long. The tube diameter is restricted by heat transfer considerations. The tubes are suspended vertically in a furnace, which may be fired from the ends or sides, the important factor being to obtain an even heat flux over the entire surface of the tubes to prevent hot-spots. Careful loading of the reactors is required to ensure an equal pressure drop in each tube to obtain good reactant distribution.

The operating conditions can vary dependent on the choice of feedstock and the product requirement. For high-purity hydrogen, a high-temperature, low pressure, high steam/carbon ratio operation minimizes methane production, but for many applications the hydrogen purity need only be 96 per cent. Steam/carbon ratio will depend on feedstock (higher molecular weight feedstocks require more steam), operating pressure and the hydrogen purity required.

The reactor effluent is partly cooled to about 400°C and passed over the high temperature shift catalyst where the water–gas shift reaction occurs:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

This reaction is exothermic and the maximum conversion to hydrogen is governed by equilibrium considerations, higher conversion being obtained at lower temperatures. The catalyst used in this application is iron oxide promoted with chromium oxide. This type of catalyst is preferred for this application, since it shows good stability under severe operating conditions, despite its activity being poor at low temperatures.

The effluent from the high temperature shift reactor can be further cooled to about 200–250°C, and the remaining CO converted to CO_2 and hydrogen in a low temperature shift reactor. The catalyst used in this application is normally copper oxide/zinc oxide/alumina. When in service, the copper oxide is reduced to metallic copper. This has high activity at low temperatures, but on its own rapidly loses surface area through thermal sintering, and it is essential to use 'spacer' support materials such as zinc oxide and alumina. Chromia and other oxides have also been used satisfactorily. The gases are further cooled and the residual steam condensed.

The carbon dioxide produced is then removed by absorption in amine or potassium carbonate solution. Typical processes used are Catocarb, Benfield, and Vetrocoke.

The residual carbon oxides are removed by reacting with hydrogen over a nickel catalyst to form methane.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

This reaction is highly exothermic and the temperature rise for a typical methanater gas composition is 74°C per 1 per cent of carbon monoxide converted and 60°C per 1 per cent of carbon dioxide converted.

A flow diagram of a typical plant for naphtha/steam reforming using carbon dioxide absorption and methanation is shown in Fig. 26.

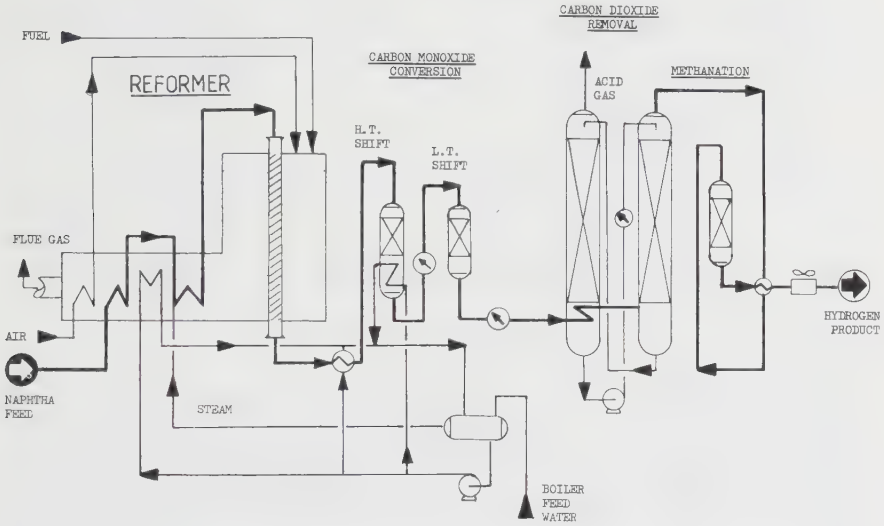


Fig. 26. Hydrogen production process using steam reforming and CO_2 absorption.

A typical equilibrium gas composition for naphtha reforming at 20.7 bars (g), 850°C and 4:1 steam/carbon ratio on a dry basis is:

CH_4	2.0% mol
CO	14.5% mol
CO_2	12.0% mol
H_2	71.5% mol

A flow diagram of a typical plant incorporating a PSA unit is shown in Fig. 27.

Partial Oxidation

An alternative method of hydrogen production is that of partial oxidation. In this type of process the heat required to arrive at the desired operating conditions is provided by combustion of part of the feed using oxygen.

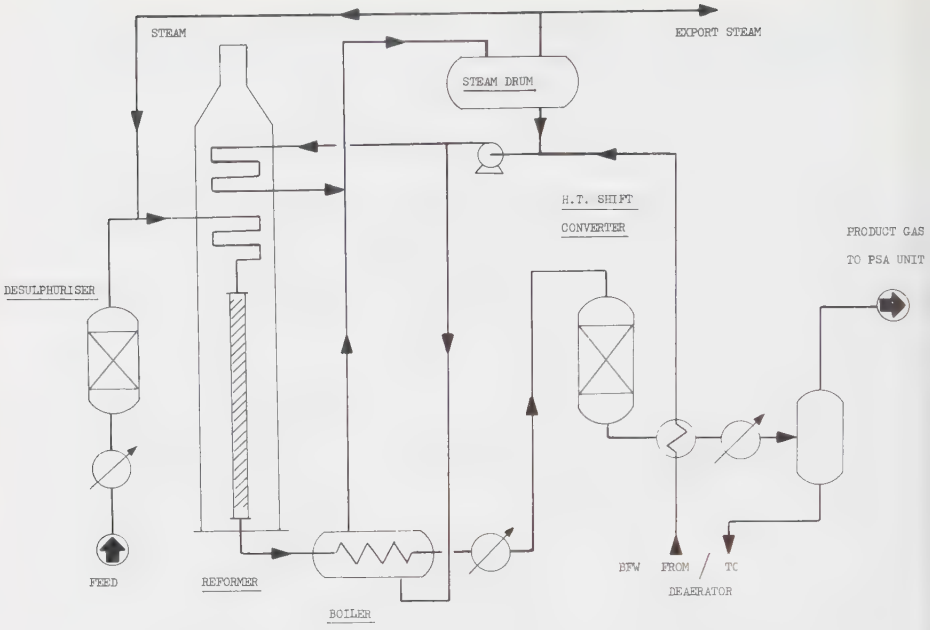


FIG. 27. Hydrogen production process using pressure swing adsorption.

Enriched air can be used if a hydrogen–nitrogen mixture is required for ammonia synthesis.

As the process is non-catalytic, it can operate with any hydrocarbon feedstock from natural gas to the heaviest residues such as asphalt and bitumen. In refinery operations the heavier feedstocks are more frequently used.

Shell and Texaco have both developed successful processes, which operate in the 30–80 bars pressure range and at temperatures between 1000 and 1600°C.

A flow diagram of the Shell Process is shown in Fig. 28. The hydrocarbon feed and oxidant (oxygen and air) are heated separately and fed to the reactor. Before entering the reaction zone, these components are intimately mixed to avoid local high concentrations of oxygen, which would otherwise give excessive temperature rises, and low concentrations which would give increased carbon formation. In simplified terms, part of the hydrocarbon is burnt, the heat produced assisting to break up the residual oil into gasifiable fractions. The combustion and cracked products react to give the desired gas mixture. To achieve the simultaneous combustion and cracking of the feedstock in the desired ratio, it is often necessary to include a 'moderator' in the reaction mixture to control the temperature. In the case where oxygen is used, steam or carbon dioxide may be used as the moderator, and where air is used the nitrogen acts as the moderator.

Carbon is produced in the process and the tendency to form carbon increases with feedstock boiling range, rising from 0.1% wt with gaseous feeds and up to 3% wt with heavy fuel oil.

The product gas leaves the reactor, carrying with it an appreciable amount of sensible heat, which is recovered in a downstream waste-heat boiler. Despite

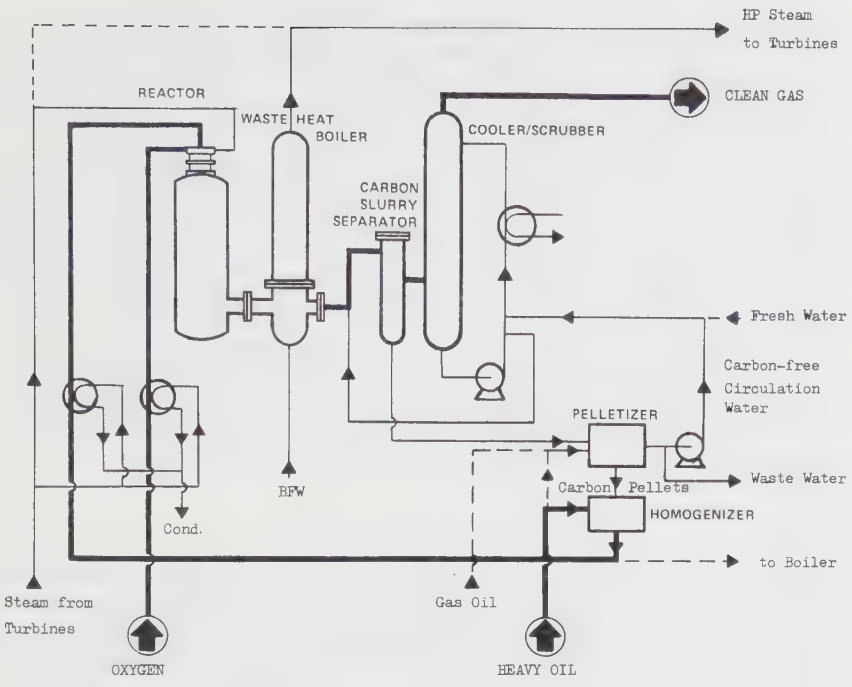


FIG. 28. Shell partial oxidation process.

TABLE XXIV

Typical Partial Oxidation Process Operating Conditions

Gasification feedstock	Dutch natural gas	Straight-run naphtha	Vacuum residue	Propane asphalt
Operating pressure, bar	60	60	60	60
Preheat temperatures, Feed °C	40/300	25	45/245	160/245
Oxygen °C	30/245	30/245	30/245	30/245
Steam °C	313	313	313	313
Feed to reactor, kg	100	100	100	100
Oxygen to reactor, Nm^3	79.2	87.9	70.6	66.6
Steam to reactor, kg	20	40	45	50
Crude gas produced, Nm^3	298	321	294	284
$(CO + H_2)$ produced, Nm^3	262	298	274	262
Composition of gas (dry), % vol				
CO_2	4.30	5.21	4.20	4.51
CO	31.71	41.29	47.21	47.74
H_2	56.28	51.45	45.81	44.22
CH_4	0.60	0.60	0.60	0.60
N_2	6.27	0.58	0.64	0.58
Ar	0.84	0.86	0.76	0.74
H_2S	—	0.01	0.75	1.55
COS	—		0.03	0.06

the presence of carbon in the effluent gas, high heat transfer rates are achieved and the gas leaves the boiler at a temperature closely approaching that of the steam produced in the boiler. If oxygen is used for gasification, about 2.8 tonnes of steam are produced/tonne of oil gasified. About 0.4 0.5 tonne of steam per tonne of feed often is used as the moderator.

The carbon is removed from the product gas, which is then purified by removal of hydrogen sulphide, before passing to shift reactors for CO conversion. Amine or carbonate absorbers are used to remove CO_2, and finally the gases are sent to a methanation reactor, as in the steam reforming process.

Typical operating conditions and reactor effluent gas compositions for different feedstocks are shown in Table XXIV.

Partial oxidation has the advantage of being able to operate on low-priced fuel oil with no restriction on sulphur content and at high pressures to reduce compression costs for high pressure processes such as hydrocracking or ammonia production. The disadvantages are the necessity for pure oxygen and therefore an air liquefaction plant is normally required.

CATALYTIC REFORMING

Prior to the First World War the octane number of straight-run naphtha from crude was improved by thermal reforming. The main improvement was as a result of cracking low octane number normal paraffins and the production of high octane number olefins. Thermal processes are, however, non-selective in their action, and are not very efficient on a yield basis in transforming low octane naphtha into high octane blending components.

Catalytic reforming, first developed in the early 1940s, is a far more efficient process for the production of the high octane number compounds required. The first such reforming process was Hydroforming, developed by M. W. Kellogg and Standard Oil of Indiana, based on a molybdenum oxide–alumina catalyst containing about 9 per cent MoO_3. The process conditions of high temperature and low hydrogen partial pressure were such that coke rapidly deposited on the catalyst. This required the catalyst to be regenerated every 4–8 hours.

The next major development was in 1949 when UOP announced the development of their Platforming process, based on platinum–alumina catalyst designed to give long on-stream times before catalyst de-activation occurred. Initially this catalyst was not regenerable *in situ*. This discovery of the advantages of platinum resulted in a large number of platinum-based reforming processes over the following few years.

The process developed along two main routes:

(a) one to achieve long on-stream process cycles,
(b) the other operating with alternating processing and regeneration periods using swing reactors.

The difference between these approaches is the rate of coke formation. In the long on-stream type, conditions of high partial pressure and low reactant residence time, necessitating high plant pressure and high recycle gas rates, respectively, are maintained to inhibit coke formation and hence slow catalyst de-activation. The other approach allowed for coke formation by the

TABLE XXV
Comparison of Semi-regenerative and Cyclic Catalytic Reformers

	Feed: Kuwait naphtha feedstock	
Specific gravity, 15/15°C	0.763	
ASTM distillation, °C		
IBP	115	
10% vol	139	
50% vol	154	
90% vol	169	
FBP	179	
Paraffins, % vol	65.1	
Naphthenes, % vol	19.4	
Aromatics, % vol	15.5	
Operation	500 psig Semi-regenerative	200 psig Cyclic
Yields, % wt		
H_2	1.0	1.9
C_1	2.2	1.1
C_2	4.5	2.4
C_3	7.2	3.4
C_4	5.8	3.5
C_{5+} Reformate	79.3	87.7
RON-Clear	95.0	95.0

incorporation of facilities for frequent catalyst regeneration. This meant that lower reaction pressures could be used, resulting in greater gasoline yields. A comparison between the product yields achieved by the two processes is given in Table XXV.

The next major development took place in 1969 with the advent of bi-metallic catalysts. These catalysts incorporate other metals (primarily rhenium) in addition to platinum. The presence of the second metal confers extra stability on the catalyst, thus slowing catalyst de-activation, and can be utilized for:

(a) longer catalyst cycle lengths,
(b) operating at lower hydrogen partial pressures to achieve higher reformate yields,
(c) operating at lower recycle gas rates, thereby saving energy, or
(d) a combination of the three above.

An added advantage has been that bi-metallic catalysts, in general, have a lower platinum content than the previous all-platinum catalysts, thus reducing the amount of capital tied up in platinum.

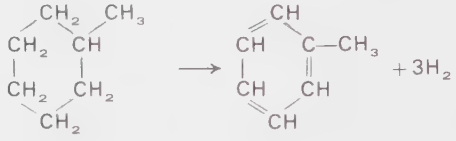
The most recent development has resulted from a new mechanical concept of the UOP Platforming process. This concept, Continuous Platforming, incorporates Continuous Catalyst Regeneration (CCR), and allows high on-stream times at very severe reforming conditions of low hydrogen partial pressure, low recycle gas rates and high reformate numbers. The first unit was commissioned in 1970 and at this time some 40 units are operating.

Chemistry

The main components of catalytic reformer feeds are paraffins, naphthenes, and aromatics. The aromatics are the high octane number components, and the prime purpose of the reforming process is to maximize aromatic production.

The main reactions are:

(a) Dehydrogenation of naphthenes to give aromatics plus hydrogen

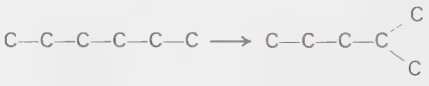


Methylcyclohexane Toluene + Hydrogen

It is evident from the above equation that reduction in unit pressure assists the dehydrogenation reaction.

(b) Isomerization

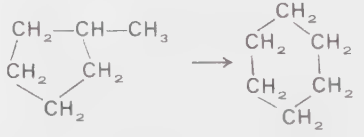
(i) Paraffin isomerization



n-Hexane 2 Methyl-pentane

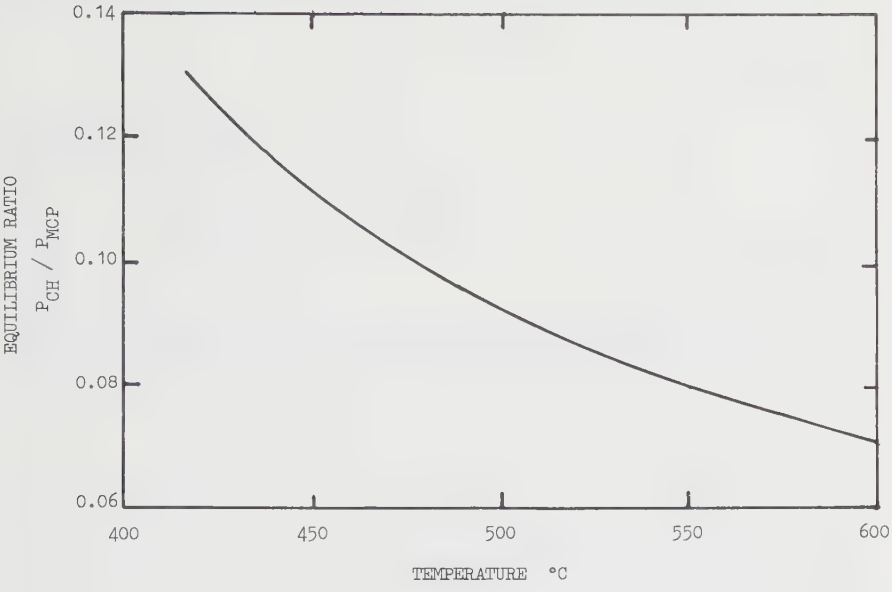
Paraffin isomerization is effective for increasing the octane number of the low molecular C_5 and C_6 paraffins only. The octane number of equilibrium mixtures of the heavier paraffin isomers decreases rapidly as the carbon number increases. In addition, the high temperatures of the reforming process are not conducive to maximizing the production of highly branched isomers.

(ii) Naphthene isomerization

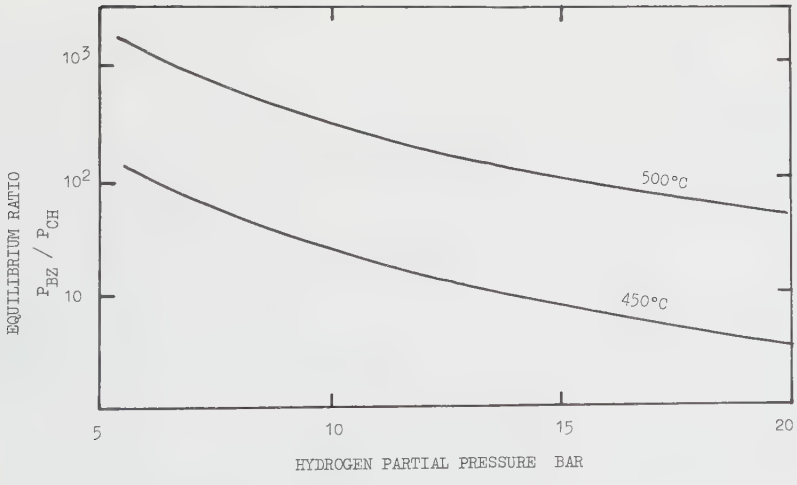


Methylcyclopentane Cyclohexane

Naphthene isomerization is assisted by lower concentrations of cyclohexane. Dehydrogenation of cyclohexane to benzene is assisted by higher temperatures, but naphthene isomerization is less favourable at higher temperatures (Fig. 29).



(a)

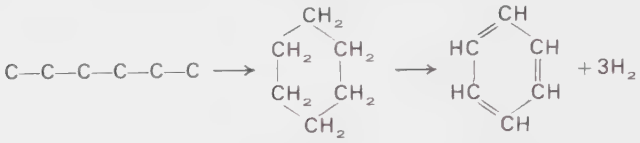


(b)

FIG. 29. Thermodynamic equilibria for (a) cyclohexane/methylcyclopentane and (b) cyclohexane/benzene systems.

(c) Dehydrocyclization of paraffins

In this case cyclization of paraffins to naphthenes followed by naphthene dehydrogenation occurs.



n-Hexane Cyclohexane Benzene

(d) Hydrocracking

The large paraffin molecules of low octane number are split into smaller molecules of higher octane number, e.g.

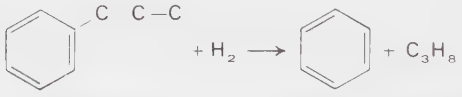
$$C_{10}H_{22} + H_2 \longrightarrow C_6H_{14} + C_4H_{10}$$

This reaction is not selective and significant quantities of hydrocarbon gases can also be formed, e.g.

$$C_6H_{14} + H_2 \longrightarrow C_4H_{10} + C_2H_6$$
$$C_6H_{14} + 2H_2 \longrightarrow C_3H_8 + C_2H_6 + CH_4$$

(e) Dealkylation

Higher aromatics can lose the side chain to form lower aromatics, e.g.



n-Propylbenzene Benzene + Propane

In the first three reactions the number of carbon atoms in the molecule remains the same and the yield is close to about 94% wt (loss of hydrogen by dehydrogenation only, no loss by isomerization). Hydrocracking and de-alkylation, however, cause a molecular breakdown and a loss in reformate yield, since these reactions produce C_1 to C_4 fragments that are outside the gasoline boiling range. C_5 and higher products have the opportunity to undergo further reactions of isomerization and dehydrocyclization.

Small quantities of aromatic polymers containing naphthalene, anthracene, and heavier compounds up to coronene are also formed. This type of reaction is probably the precursor of coke which deposits on the catalyst surface and de-activates the catalyst.

Naphthene dehydrogenation and paraffin dehydrocyclization reactions are strongly endothermic, whilst hydrocracking and de-alkylation are exothermic.

Isomerization is mildly exothermic. The heats of reaction of some of the reactions are quoted below.

	Heat of Reaction (Kcal/g mole)	
	C_6	C_7
Paraffin hydrocracking	13.5	13.5
Paraffin isomerization	2.3	2.3
Paraffin dehydrocyclization (Cyclohexanes)	−12.9	−10.7
(Cyclopentanes)	−16.7	−15.2
Naphthene isomerization	−3.8	−4.5
Naphthene dehydrogenation	−52.3	−51.5

The reactions involving dehydrogenation are strongly influenced by both temperature and hydrogen partial pressure. Aromatic formation is favoured by high temperature, low hydrogen partial pressure, and increasing carbon number of reactant. This effect is shown clearly in Figs 30 and 31 for the n-hexane/benzene/hydrogen and n-heptane/toluene/hydrogen systems, respectively.

As can be seen by studying the above reactions, the choice of process operating conditions must be a compromise between a high conversion to aromatics, achieved at low hydrogen partial pressures, and the prevention of coke deposition on the catalyst, promoted by high hydrogen partial pressures to achieve long catalyst on-stream periods. As mentioned earlier, the advent of bi-metallic catalysts and the CCR Platforming process has gone some way to achieve the high conversion to aromatics without suffering the penalties of rapid catalyst de-activation.

Feedstocks

Catalytic reformer feedstocks are saturated (i.e. not olefinic) materials boiling in the range 75°C–190°C. Lower boiling fractions containing C_5 components, which are not amenable to reforming, are preferably passed to an isomerization process for upgrading. In the majority of cases the feedstock will be a straight-run naphtha. By-product low octane naphthas from other processes may also be processed after treatment for removal of olefins and other contaminants. Hydrocracker naphthas are particularly suitable since they contain substantial quantities of naphthenes.

Naphthas from different crude sources vary considerably in hydrocarbon type as shown below in Table XXVI.

TABLE XXVI

Composition of 95–175°C Naphthas (% wt)

Crude	P	N	A
Kuwait	64.6	20.7	14.7
Iranian Light	51.8	31.2	17.0
Forties	42.6	41.1	16.3
Nigerian Forcados	28.5	54.0	17.5

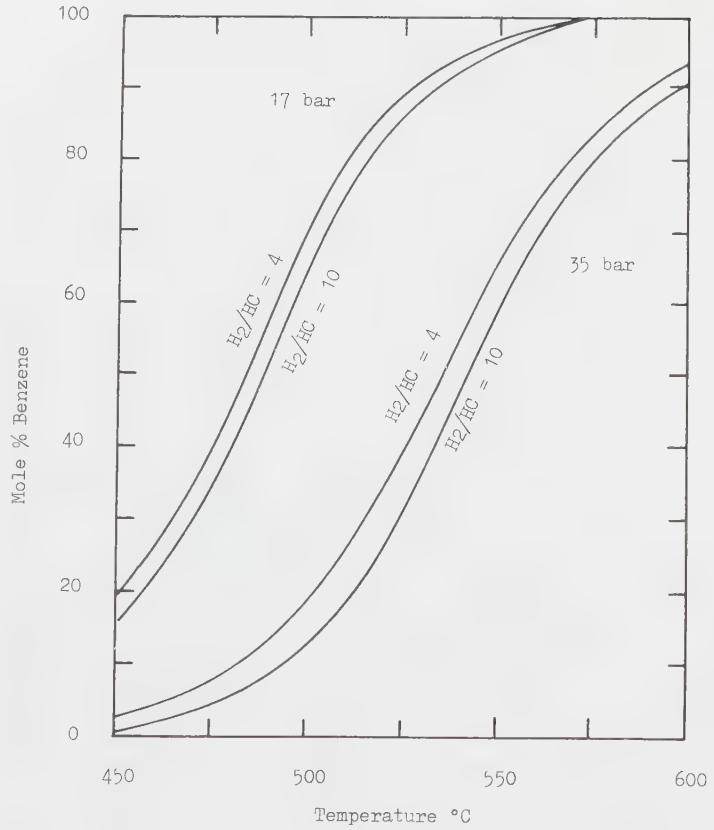


FIG. 30.

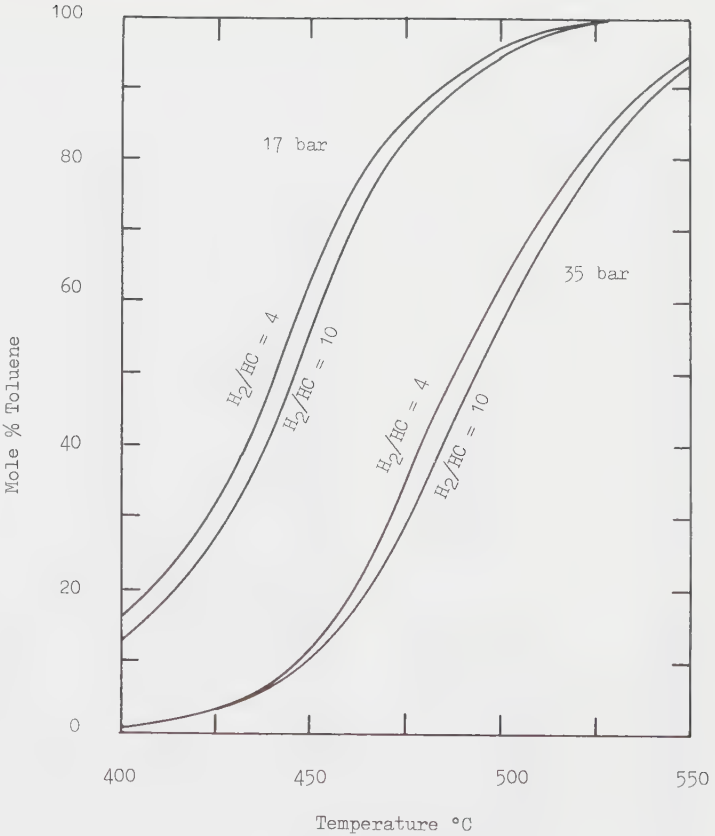


FIG. 31.

Equilibrium distribution for the n-hexane/benzene/hydrogen and n-heptane/toluene/hydrogen systems.

The reformate yield of a given octane number and specific operating conditions varies with the naphthenicity of the feedstock. High naphthenes feeds, which readily convert into aromatics, are the easiest to reform and give the highest reformate yields. The more paraffinic stocks, which depend more on dehydrocyclization, isomerization, and hydrocracking reactions, require more severe operating conditions and give lower reformate yields than the naphthenic stocks. This difference becomes more marked at the higher octane numbers as shown in Fig. 32.

Feedstock endpoint is usually limited to temperatures in the range 175°C to 190°C, dependent on the unit operating severity and crude type. Increasing coke deposition occurs on the catalyst as the endpoint of the feedstock increases. Reforming also causes an increase in the liquid product endpoint of some 15°C above that of the feed. Limiting the feed endpoint can avoid a redistillation of the product to meet the normal gasoline endpoint specification of 204°C maximum.

Reforming catalysts are easily poisoned, particularly the metal components,

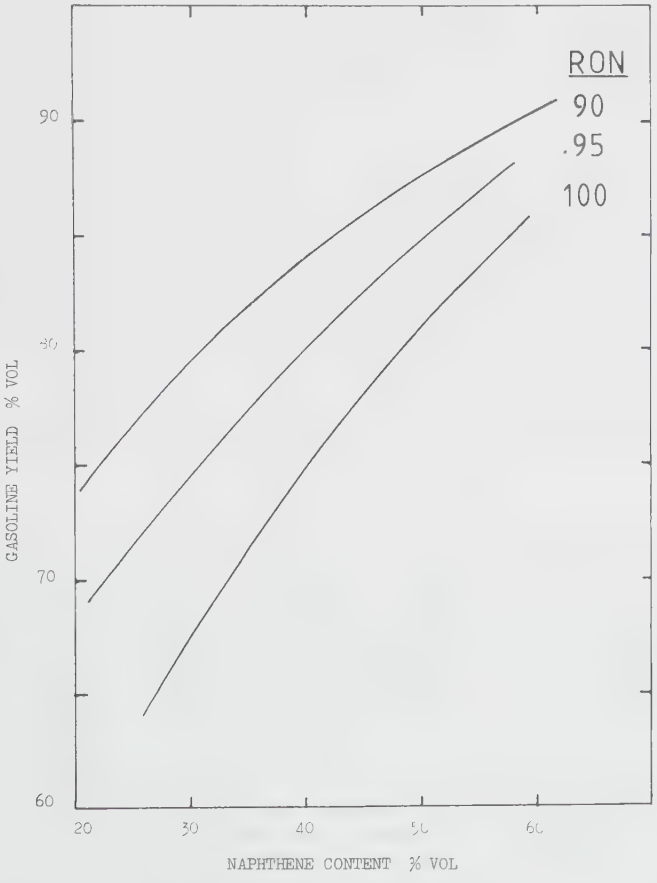


FIG. 32. Effect of feedstock naphthene content on catalytic reformate yield.

and it is therefore necessary to limit contaminants in the feed to a catalytic reformer. The most important of these are as follows:

Sulphur

With the operating conditions used in catalytic reforming, sulphur compounds present in the feed are readily converted into hydrogen sulphide, which unless removed, will build up to a high concentration in the recycle gas. Hydrogen sulphide reacts with the platinum on the catalyst to form platinum sulphides causing a decrease in catalyst activity for the metal catalysed dehydrogenation and dehydrocyclization reactions. Sulphur may be considered a temporary catalyst poison, provided that higher temperature is not used to compensate for the loss in catalyst activity to maintain product octane number. When the hydrogen sulphide is removed from the recycle gas the platinum sulphide will be reduced to platinum. If reactor temperatures are increased, however, catalyst coking will be more rapid, resulting in more rapid catalyst deactivation, and in these circumstances sulphur would act as a permanent poison.

In the first catalytic reformers, hydrogen sulphide was removed from the recycle gas stream by absorption in, for example, diethanolamine. Units built from 1960 onwards usually have the sulphur removed from the feedstock by desulphurization in a separate hydrotreating unit using nickel–molybdenum or cobalt–molybdenum catalysts. The new bi-metallic reforming catalysts are more sensitive to sulphur than the older mono-metallic catalysts and it is essential to reduce the sulphur in the feedstock to 0.5 ppm.

Sulphur control is considered extremely important by some process licensors, and a recent development has been the incorporation of proprietary sulphur absorption techniques in the reformer feed after conventional feed hydrotreatment. This will reduce feed sulphur levels to 0.1 ppm, and is claimed to give better catalyst stability, resulting in longer catalyst cycle lives and better reformate yields.

Additional benefits of feed desulphurization to low levels is the elimination of H_2S corrosion problems in heaters and reactors.

Nitrogen

Organic nitrogen compounds are readily converted into ammonia under reforming conditions. The ammonia produced neutralizes acid sites on the catalyst, and thus depresses the activity for isomerization, hydrocracking and dehydrocyclization reactions. Extremely small quantities of nitrogen can have an adverse effect and a limit of 0.5 ppm in the reformer feed is specified. Normally straight-run feedstocks do not present serious problems, since the majority contain < 1 ppm in the reformer feed fraction. In addition, hydrotreatment to remove sulphur will also remove some nitrogen. However, feedstocks derived from thermal processes such as coking and visbreaking and catalytic cracking may contain nitrogen up to 50 ppm, dependent on the nitrogen content of the feed to the process. Removal of this quantity of nitrogen will require high pressure hydrogenation over a nickel–molybdenum alumina catalyst.

The presence of nitrogen in the feed causes the additional problem of deposition of ammonium chloride in the reformer stabilizer. This can result in loss of fractionation efficiency, or even blockages.

Metals

Reforming catalysts are extremely sensitive to arsenic, copper, and lead poisoning. Arsenic can have an effect at a level of a few parts/10^9, and copper and lead at 20 to 30 parts/10^9 in feed. Arsenic is present probably because of contamination of the crude oil well with arsenic compounds which have been used as inhibitors during acid treatment of the well to increase production. Feedstocks derived from certain shale oils also contain arsenic. Lead is the most common poison, entering the feed through contamination with TEL or TML in storage, or more usually by the processing of leaded slops through the crude oil distillation unit. These contaminants are normally removed without difficulty if the reformer feed is desulphurized, and are deposited on the desulphurization catalyst, which is less sensitive than the platinum-containing reforming catalyst. Care should still be taken, however, as the desulphurization catalyst will eventually cease to retain the metals, and they will then deposit on the reforming catalyst. If leaded slops are processed regularly, particularly at levels in excess of 100 parts/10^9 on feed, careful monitoring of reformer feed lead levels should be carried out.

Water

Control of feed water content, and hence of the unit recycle gas, is necessary to obtain optimum operation of the reforming unit, as discussed later under water content. A sudden rise in water content will result in increased catalyst hydrocracking activity, giving higher C_3 and C_4 production with a commensurate reduction in hydrogen make and reformate yield.

Chlorine

Organic chloride in the feed can, like water, result in increased hydrocracking activity. This will be discussed later with the effect of water.

Catalysts

From reference to the chemistry of the reforming process above, it can be seen that a reforming catalyst must be dual function in nature. A metal function, platinum in this case, promotes dehydrogenation and hydrogenation reactions which are important for the production of aromatics, participating in hydrocracking and rapid hydrogenation of coke-forming precursors. An acid function promotes isomerization, the initial step in hydrocracking, and participates in paraffin dehydrocyclization. The balance between these two forms of catalytic activity is most important. The catalyst support, normally alumina, is also important. The surface area of this support should be high, on fresh catalyst in excess of 160 m^2/g (measured by nitrogen absorption techniques), so that the active catalytic components can be widely dispersed on the support in order to maximize catalytic activity.

The platinum content of mono-metallic reforming catalysts is normally in the range 0.25 to 0.8% wt. At higher levels there is a tendency for naphthene ring opening and demethylation to occur, whilst at lower levels the catalysts are less resistant to the presence of poisons in the feedstock. Platinum is extremely expensive (about £260/tr oz at producer prices) and the metal content of the catalyst represents a substantial amount of capital tied up. Fortunately, bi-metallic catalysts are now available, which have reduced the platinum requirement down to the range 0.2 to 0.4% wt and, in addition, provide increased catalyst stability against de-activation under normal unit operating conditions. The most common metal used, rhenium, is present in the range 0.2 to 0.6% wt, and is relatively cheap (about £380/kg). Normally the higher metal levels are used for more severe process requirements.

The acid activity is obtained by the use of halogens or silica incorporated in the alumina base. The majority of catalysts in use today use chlorine as the acid component, in the range 0.8 to 1.2% wt on catalyst.

According to patents, catalysts can be prepared by precipitating an alumina hydrogel by reacting ammonium hydroxide with aluminium chloride and washing the gel until the chloride level is less than 0.1% wt. The gel is filtered and re-slurried, and the correct quantity of chloride added. The platinum is then added in the form of chloroplatinic acid solution treated with hydrogen sulphide. After mixing, the gel is dried, pelleted (in its broadest sense) and calcined at about 550°C.

Another patent claims the importance of the presence of a large proportion of alumina trihydrate in the catalyst base. The alumina is precipitated from aluminium chloride with ammonium hydroxide and the gel, after washing to remove chloride to less than 0.2% wt, is aged for several days at pH 8. It is claimed that the resultant alumina base has a larger proportion of its available surface area in pore sizes 100–1000 Ångstrom units, and that this type of alumina gives catalysts showing a lower rate of activity decline under reforming conditions.

All reforming catalysts are now regenerable, i.e. carbon deposited on the catalyst can be removed by combustion under controlled conditions to restore catalyst activity. If catalysts have been poisoned by metal deposition they are unregenerable and have to be replaced. The spent catalyst is returned to specialist firms for platinum recovery.

Platinum catalysts will not return to full initial activity with carbon removal alone. Under certain conditions the platinum present on the catalyst agglomerates into large crystallites, which reduce the intrinsic metal activity of the catalyst. Over the last decade, process licensors have developed proprietary techniques which allow the platinum to be redistributed over the alumina base into the initial finely divided state. This has resulted in catalysts capable of lasting for many years.

Process Variables

Temperature

Normally reactor inlet temperatures lie in the range 470 540°C. At temperatures below 470°C, reaction rates are too slow, and above 540°C, the

rate of hydrocracking becomes excessive, with resultant loss in reformate yield. Thermal cracking also occurs at around this temperature leading to rapid coke deposition on the catalyst. Increasing the reaction temperature will result in an increase in reformate octane number because of the increased rates of reaction. As the catalyst de-activates under normal process conditions, reactor inlet temperatures must be increased to maintain reformate octane number at the required level. A normal process operating cycle allows for a temperature increase of about 20°C between start and end of run under fixed operating conditions.

Space velocity

Space velocity, defined as the volume of oil processed per hour per volume of catalyst, is chosen depending on the hydrocarbon types present in the feed and the octane number required. With highly naphthenic stocks, high space velocities can be used as naphthene dehydrogenation reactions are rapid. However, more paraffinic stocks require lower space velocities to achieve the desired octane number as these rely on dehydrocyclization reactions which are much slower. Increases in reactor temperature do of course increase the rate of all reactions, and so the desired severity to achieve a given octane number is a combination of both temperature and space velocity effects, with the temperature limitations outlined above. Space velocities for motor gasoline production are usually in the range 1–2, but for aromatics production from selected naphthenic feedstocks even higher space velocities can be used.

Pressure

Pressure affects both dehydrogenation and hydrocracking reactions. Increase in reactor pressure increases the degree of hydrocracking, but adversely affects the equilibrium aromatic formation. Lowering pressure has the converse effect. Higher pressure reduces the carbon deposition on the catalyst and slows catalyst de-activation.

Prior to the advent of bi-metallic catalysts, reaction pressures were in the range 400–600 psig (27.5–41.5 bars). Now it is possible to design units in the pressure range 125–300 psig (8.6–20.5 bars).

As mentioned previously, a reduction in unit pressure will increase the yield of C_5 plus reformate and hydrogen production, and reduce the production of light hydrocarbon gases. This effect is illustrated in Fig. 33.

Hydrogen–hydrocarbon ratio

Hydrogen to hydrocarbon ratio (mols of hydrogen in recycle gas/mol of feedstock processed) affects reactant residence time, and at lower values the hydrogen partial pressure in the reactor. With mono-metallic, platinum catalysts, the hydrogen–hydrocarbon mol ratio was in the range 5–10:1, dependent on the severity of operation required and the unit operating pressure. Regenerative processes using swing reactors were in the range 3 5:1. With the advent of the more stable bi-metallic catalysts it has been possible to operate at lower hydrogen–hydrocarbon mol ratios in the range 3.5–7:1. In the

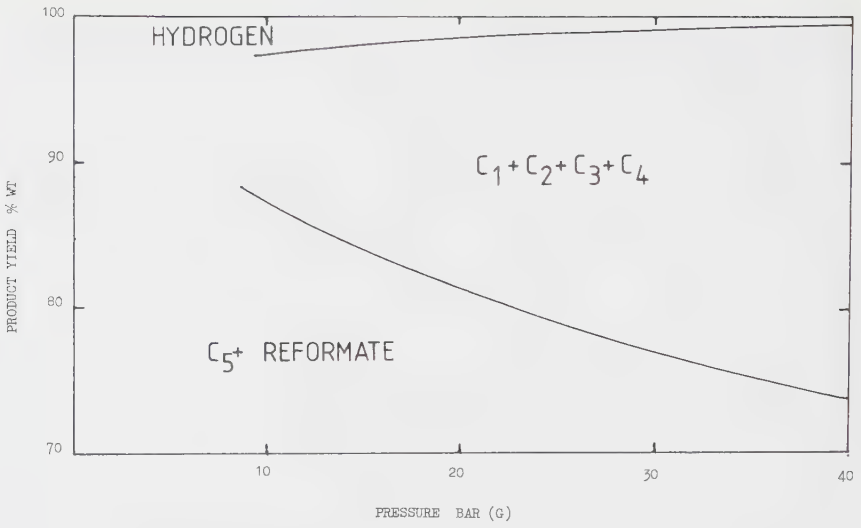


FIG. 33. Effect of reactor pressure on catalytic reformer yields.

case of CCR units with the ability to regenerate the catalyst on a continuous basis even lower hydrogen-hydrocarbon ratios can be used.

There is an economic incentive to reduce the hydrogen–hydrocarbon ratio to a minimum consistent with adequate catalyst cycle life. Since the oil crises of 1973 and 1979, the high cost of circulating the gas through the unit and heating the gas to reaction temperatures has become a significant factor. A comparison of approximate recycle gas compressor brake horse-power and charge heater requirements at varying hydrogen–hydrocarbon ratios is given in Table XXVII.

Water content

Water entering the unit with the feed will pass over the catalyst in the reactors, and will be in equilibrium between the unit recycle gas and the product liquid in the separator vessel. The amount of water present passing over the catalyst will therefore be the sum of that in the feed and in the recycle gas.

The immediate effect of increasing the water content of the reactor feed is to increase the hydrocracking activity of the catalyst. This, if allowed to continue, will result in a loss of reformate yield and a reduction in hydrogen production. It will also lead to a reduction in hydrogen concentration in the recycle gas due

TABLE XXVII

Influence of Recycle Gas Rate on Energy Requirements
Unit Feed Rate 10 000 BPSD

Hydrogen–hydrocarbon, mole ratio	6:1	8:1	10:1
Charge heater duty, 10^6 Btu/h	52.9	66.0	77.0
Recycle gas compressor duty, bhp	1 600	2 150	2 700

to production of extra C_1–C_4 hydrocarbons. Catalyst life will suffer unless the recycle gas rate is increased to maintain hydrogen partial pressure and also due to the increased production of coke precursors. Some water is required with most catalysts, however, as high demethylation activity has been reported with water contents in the feed lower than 10 ppm.

When catalysts contain chloride as the acid function promoter, the presence of excess water will tend to strip chloride from the catalyst. The long-term effect of too much water will be a reduction in hydrocracking activity as opposed to an increase in the short term. With these types of catalyst it is essential that a balance between the metal and acid functions of the catalyst is maintained. To this end, the chloride content on the catalyst is maintained at the desired level, and this is achieved by maintaining the water content in the 10–30 ppm mol range in the recycle gas and adding small quantities of an organic chloride (e.g. propylene dichloride) to replenish the chloride removed by the water should there be insufficient naturally occurring chloride in the feed. Feed chloride levels should normally be in the range 0.5–2.0 ppm weight, depending on the optimum recycle gas water content for a particular catalyst.

Feedstocks containing too much chloride will result in the catalysts having excessive hydrocracking activity. If this should be the case, steps must be taken to eliminate the source of high chlorine in the feed, and feedstock water should be increased to remove the excess chloride from the catalyst. Reaction temperatures should be reduced whilst this operation is carried out.

Processes

As mentioned earlier the catalytic reforming process developed along two separate paths, those designed for long on-stream runs between catalyst regenerations, and those in which catalyst regeneration forms part of the processing cycle. In addition, over the last decade the UOP Continuous Catalyst Regeneration (CCR) process has been developed. These three types of process will be described separately below.

Catalytic reforming with long on-stream runs between catalyst regeneration (semi-regenerative)

Processes in this category include the original reforming process—UOP Platforming, Sinclair Baker Reforming, now Engelhard, the Engelhard Magnaforming process and the Chevron Rheniforming process. All the plants used in these processes are similar in principle, the differences being in the type of catalyst employed and the operating and regeneration procedures used. Process operating conditions are normally in the following range:

Reaction pressure	10–40 bars (g)
Temperature	460–540 °C
Liquid hourly space velocity	1–3 v/v/h
Hydrogen/hydrocarbon, mole ratio	2:1–8:1

A flow diagram of a typical Platformer or Rheniformer is shown in Fig. 34. Feed, which has been desulphurized in a naphtha desulphurizer or distillate

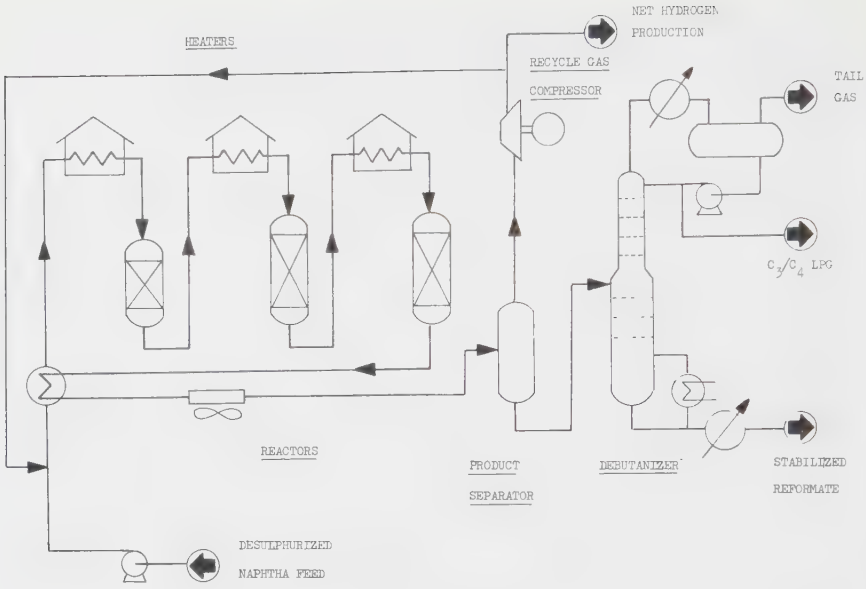


FIG. 34. Semi-regenerative catalytic reforming process.

hydrotreater, is pretreated together with hydrogen-containing recycle gas, first by heat exchange with reactor effluent and then in a fired heater before passing to the first reactor. The prime reaction in this reactor is naphthene dehydrogenation, which is endothermic and rapidly drops the reaction temperature. The effluent from the first reactor is reheated in a reactor interheater before entering the second reactor. Further dehydrogenation and some paraffin dehydrocyclization take place, again dropping the reaction temperature. The effluent from the second reactor is reheated in a second reactor interheater before passing to the third reactor where the slower hydrocracking and paraffin isomerization reactions occur predominantly. The effluent from the final reactor is heat exchanged with reactor feed and cooled to near ambient temperature in a reactor products condenser, and passes to a separation vessel to separate recycle gas from liquid product. The recycle gas, containing from 55 to 90 per cent hydrogen depending on feed composition and operating severity, is compressed and passes back to the feed. Excess gas produced in the process is vented from the unit and is utilized in other processes, e.g. hydrofining or other hydrogen-consuming processes. The liquid from the separator passes to a distillation column, known as the stabiliser or debutanizer, to remove the C_4 and lighter material. The stabilizer reformate is then passed to storage for blending into gasoline.

In most units there are three reactors, but frequently there are four, particularly when processing highly naphthenic feedstocks or when the unit is designed for lower pressure operation in order that the large amount of heat required by the endothermic nature of the naphthene dehydrogenation reaction can be readily supplied. The way in which the catalyst is split between the various reactors is subject to wide variations. All units have a small first

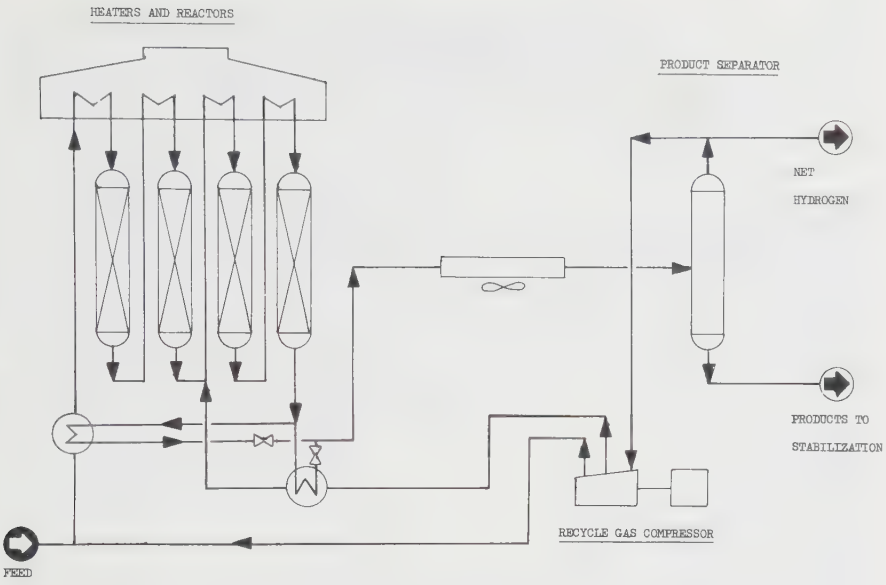


FIG. 35. Engelhard Magnaforming process.

reactor since naphthene dehydrogenation is rapid and takes place at a high space velocity. The second reactor is larger than the first and the third reactor larger still. Some of the older high pressure units have catalyst distributed in the ratio 1:2:2 or 1:2:4, whilst other newer lower pressure units have the catalyst distributed in the ratio 1:1.5:2.5:5.

Engelhard have claimed to optimize the catalytic reforming reactions in their Magnaforming process (Fig. 35). A typical design consists of a four-reactor system using a highly skewed catalyst distribution with gas recycle introduced ahead of the first and third reactors. The reactor inlet temperatures follow an ascending pattern, with the inlet temperatures to the first two reactors held constant through the whole process cycle. The mild conditions in the first two reactors, low temperatures and high space velocity, minimize paraffin and naphthene cracking, thereby contributing to improved liquid product selectivity. At these low temperatures, catalyst fouling is reduced and lower recycle gas rates may be used. The remaining reactors are operated at higher gas recycle rates to minimize fouling at the higher temperatures required. The recycle gas split is normally provided by a single side take off centrifugal compressor. The greatest yield advantages are said to be obtained with paraffinic stocks, with the least improvement shown by heavy hydrocrackate feedstocks high in naphthenes. Typical operating conditions and yield data for various feedstocks are given in Table XXVIII.

With these processes, the catalyst de-activation takes place relatively slowly and reactor inlet temperatures are increased to maintain the reformate octane number at the desired level. Higher temperatures favour the cracking reactions, and as carbon deposits on the catalyst it loses selectivity; eventually there is a progressive decline in reformate yield with a corresponding increase in C_1–C_4 gas production. Gasoline yields can fall by up to 5% vol on feed, but it

TABLE XXVIII
Typical Magnaforming Data

	Feed type			
	Straight-run		Heavy hydrocrackate	
Feedstock data				
Specific gravity, 15/15°C	0.760		0.760	
ASTM distillation, °C				
IBP	103		94	
10% vol	117		116	
50% vol	139		142	
90% vol	170		176	
95% vol	176		188	
FBP	188		198	
Paraffins, % vol	51.5		32.0	
Naphthenes, % vol	33.8		48.0	
Aromatics, % vol	14.7		20.0	
RON-Clear	43.5		69.5	
Operation conditions				
Average reactor pressure, bars (g)	14.0		14.0	
WHSV, w/w/h	2.0		2.5	
H_2:HC, mol ratio				
To R-1	2.5:1		2.5:1	
To R-3	5:1		5:1	
Reactor inlet temperatures, °C				
R1 and R2	470 490			
R3 and R4	510		507	
Magnaforming yields	wt %	vol %	wt %	vol %
H_2	2.3	—	2.4	—
C_1	1.2	—	0.7	—
C_2	2.2	—	1.5	—
C_3	3.1	—	2.0	—
iC_4	1.7	2.3	1.0	1.5
nC_4	2.5	3.2	1.6	2.3
C_{5+} reformate	87.0	80.7	90.8	85.0
RON-Clear	100		102	

is normal to consider regenerating the catalyst before the yield decline reaches this level. The reasons for this are twofold. First, the loss of reformate becomes economically unacceptable and, secondly, it is preferable to regenerate the catalyst before it becomes completely de-activated to obtain the best ultimate catalyst life. Ultimate lives in excess of 200 bbl of feed/lb of catalyst with a mono-metallic catalyst and 400 bbl of feed/lb with bi-metallic catalysts can be obtained.

Regeneration is carried out by carefully burning off the coke on the catalyst, avoiding excessive temperatures which might otherwise damage the structure of the catalyst base. The usual procedure is to circulate inert gas over the catalyst at about 400°C and 7 bars (g), using the recycle gas compressor. Air is introduced to the recirculating gas stream to give an oxygen content of about 0.7% vol at the reactor inlet. The temperature rise across the burning front should not exceed 56°C. When the burning front has passed through all the

reactors, the inlet temperatures are raised to 430°C and then the oxygen content is increased to 2% vol until all the carbon is burnt off.

Following the carbon burn, proprietary techniques are used to redistribute the platinum before the catalyst is ready for the new process cycle.

Catalytic reforming with cyclic regeneration

The processes using this type of operation are Powerforming (Esso Research and Engineering Co.) and Ultraforming (Amoco). The difference between this type of operation and the previous method is that the catalyst is allowed to function under much more severe operating conditions, resulting in rapid catalyst de-activation due to coke deposition, and must therefore be regenerated at more frequent intervals. Lower pressures and lower recycle gas rates are employed offering the advantages of:

(a) Higher reformate yields,
(b) Higher hydrogen yields,
(c) Lower charge heater fuel and recycle gas compressor power requirements.

The layout of a typical unit is shown in Fig. 36. It is essentially similar to the semi-regenerative type of process described previously, except that an extra reactor is provided so that at all times the catalyst in one reactor is regenerating, whilst the remaining reactors (three or four) remain in service. Extra pipework and valving are required for the regeneration gas circuit, and special attention has to be paid to the safety of the system to permit isolation of

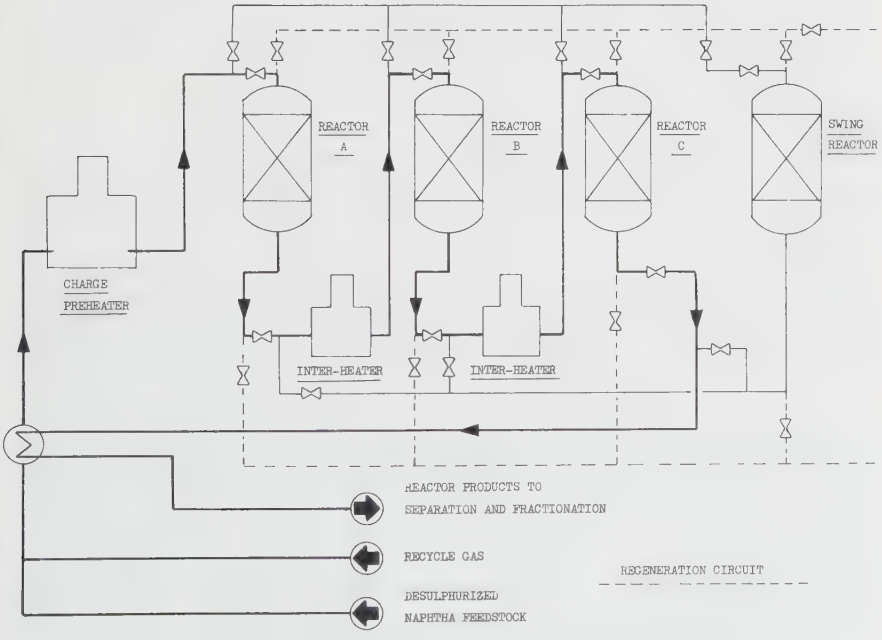


Fig. 36. Exxon Powerforming process with cyclic catalyst regeneration.

reactors under process flow from that on regeneration, and whilst substituting the reactor to be regenerated from that having undergone regeneration. A considerable increase in unit complexity is required.

The regeneration procedure is similar to that used on semi-regenerative units as described previously, and usually takes about 16–20 hours. With a four-reactor system (three on-stream, one regenerating) the minimum on-stream time for any reactor must be 48–72 hours. Robust catalysts have been developed which, it is claimed, have been regenerated up to 500 times.

Typical Ultraforming data are given in Table XXIX.

TABLE XXIX
Ultraforming Data

Feed properties	Case 1	Case 2	Case 3
ASTM distillation, °C			
IBP	114	93	89
10% vol	128	110	104
50% vol	151	128	130
90% vol	180	157	166
FBP	204	183	184
Paraffin, % vol	35.0	51.3	68.5
Product yields			
Hydrogen, SCF/bbl	1 310	1 000	590
C_1-C_3, % wt	4.1	9.7	15.7
C_4, % vol	5.5	6.9	11.0
Gasoline, % vol	82.2	76.8	69.2
RON-Clear	102	100	100

Continuous catalytic reforming

There are two processes using this type of operation, namely, UOP's continuous catalyst regeneration (CCR) platforming and the IFP continuous reforming process. They differ in unit configuration and the method of regeneration.

The UOP process is shown in simplified form in Fig. 37. The hydrocarbon and recycle gas flows are essentially the same as in a conventional fixed bed, semi-regenerative operation. Instead of the reactors being located side-by-side as in a conventional reformer, they are stacked one on top of the other to facilitate catalyst flow. Freshly regenerated catalyst flows from the top of the first reactor by gravity through the first reactor, then to the second reactor through a number of interconnecting pipes to the next reactor and so on until it reaches the bottom of the terminal reactor. The coked catalyst, containing about 5% wt carbon is then lifted to the CCR unit and the carbon burnt off. The catalyst circuit is completed by lifting the regenerated catalyst back to the top of the first reactor. The coke on catalyst retains an essentially constant profile and the catalyst remains close to fresh activity at all times. Thus continuous platforming is able to maintain a constant quality reformate and hydrogen-rich excess gas at high yield.

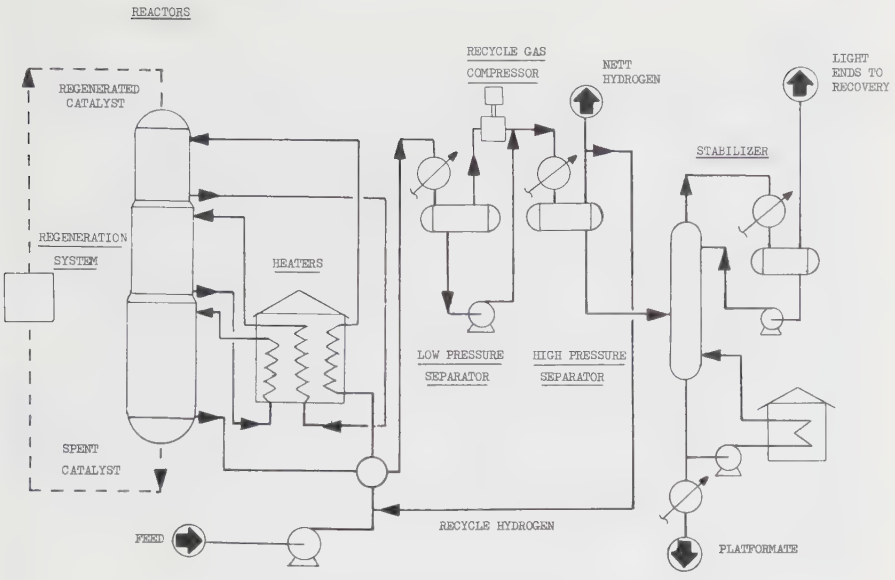


FIG. 37. UOP continuous catalyst regeneration platforming process.

The main features of the process are the low pressure operation to maximize reformate yield, the low recycle gas rates employed which minimize utility requirements, and the ability to run at higher temperatures to minimize catalyst requirements. To achieve the low pressure operation, a number of new engineering features have been adopted to minimize the overall pressure drop in the system. These include radial flow reactors, close-coupling of the reactor stack to the charge and inter-reactor heaters, the use of long-radius elbows on all bends, single-pass, vertically mounted, counter-current feed/effluent heat exchangers, and finally, the use of so-called 'wicket' type heaters.

A comparison between semi-regenerative and continuous platforming is shown in Table XXX.

Part of the increased reformate yield is due to being able to operate continuously at a lower pressure under which the semi-regenerative unit catalyst would de-activate too rapidly for the operation to be economic.

The flow diagram of the IFP process is shown in Fig. 38. In this case, the reactors are located side-by-side as in conventional semi-regenerative units.

TABLE XXX

Comparison Between Semi-regenerative and Continuous Platforming

Basis: 20 000 BPSD Arabian Light Naphtha, 100 RON-Clear			
Platformer mode		Semi-regenerative	Continuous
C_{5+} reformate	% vol on feed	73.2 (mid-life)	77.2 (steady-state)
H_2:HC ratio	molal	H*	0.5H
LHSV	v/v/h	L*	2 × L

* H and L are units of H_2:HC ratio and LHSV, respectively.

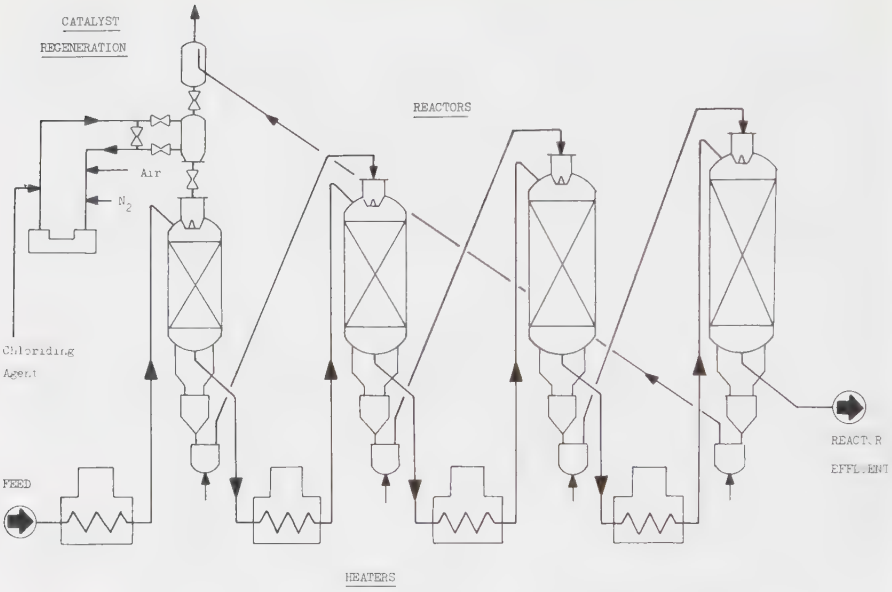


FIG. 38. IFP continuous catalytic reforming process.

The catalyst flows by gravity through the first reactor and is then lifted to the top of the second reactor, and so on. The catalyst from the bottom of the terminal reactor is lifted to the top of the regeneration section and passes to a storage hopper. The catalyst is then passed batch-wise to a regeneration vessel and is regenerated as if it were in a conventional reformer. After regeneration, the catalyst is sent to a second storage hopper and is then taken as required to the top of the first reactor.

TABLE XXXI
Comparison of HC-Platforming and Platforming

Feedstock	104 202 °C Mid-Continent US naphtha	
RON	85.5 clear	
Separator pressure	18.5 bars (g)	
Yields, % wt	HC Platforming	Platforming
H_2	0.96	1.63
C_1	0.44	0.70
C_2	0.39	0.90
C_3	2.51	2.40
iC_4	6.27	1.26
nC_4	3.20	1.85
C_{5-}	86.23	91.26
C_{4+}	95.70	94.37
Platformate distillation		
IBP, °C	49	52
10 °C	79	99
50 °C	121	130
90 °C	158	166
FBP, °C	203	219

HC platforming

This is a modification of the conventional platforming process, in which an extra reactor is incorporated in the same recycle gas circuit as the reformer. The reactor is located between the combined feed/effluent exchanger and the reactor charge heater. This reactor, operating under mild hydrocracking conditions, cracks higher molecular weight hydrocarbons, primarily paraffins, to give high yields of iso-paraffins of lower boiling point and, especially, isobutane. The use of this process allows higher boiling point naphthas to be fed to the reformer without de-activating the main reforming catalyst, and without the resultant reformate endpoint being outside normal gasoline blending specifications.

A comparison between HC-platforming and conventional platforming is given in Table XXXI. The disadvantages of HC-platforming are the reduced hydrogen and C_{5+} reformate production. The advantages are increased isobutane production, particularly where there is a requirement for isobutane for alkylation, the ability to process higher endpoint feedstocks, and finally the increased volatility of the HC platformate.

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15

Alkylation, Isomerization, Polymerization, Hydrotreatment and Sulphur Production

By L. J. McPHERSON and M. F. OLIVE

ALKYLATION

Introduction

Alkylation, in a petroleum refining context, refers to a process used for producing high-octane motor fuels by combining light olefins with isobutane in the presence of a strong acid catalyst. Alkylation is also used in petrochemicals manufacture for producing materials such as ethylbenzene and isopropylbenzene by reacting selected olefins with aromatics.

Alkylation was discovered in 1932 by Ipatiev and Grosse who found that light olefins would react with certain iso-paraffins in the presence of a boron trifluoride catalyst promoted with water or hydrogen fluoride. It was soon afterwards reported by Ipatiev and his co-workers that aluminium chloride promoted with hydrogen chloride was also an effective alkylation catalyst, and this remains in common use today for producing alkyl aromatics.

The alkylation process for producing gasoline is based almost entirely on the use of sulphuric acid or hydrogen fluoride as catalyst. Sulphuric acid alkylation was discovered simultaneously in 1936 by Birch, Fidler, Pim, and Tait at the British Petroleum Research laboratories in England and by Visser working at the Bataafsche Petroleum Mij. laboratories in Holland. The use of hydrogen fluoride as an alkylation catalyst was patented by Grosse and Lewis in 1938.

In the Second World War, the alkylation process was to assume great importance in the manufacture of high-octane aviation gasoline for military purposes. However, in later years, after the development of the jet engine, this use declined and today alkylate is used almost entirely as a motor gasoline blending component.

The olefins used in isobutane alkylation are usually the propene and butenes produced by the catalytic cracking process, although in some cases the C_3 and C_4 olefins from a steam cracker or other thermal cracking processes are also included. Alkylation with pentenes from a catalytic cracking unit is also known, but this is less common.

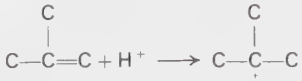
Alkylation Reactions

Basically, the alkylation reaction results in the formation of iso-paraffins containing the sum of the number of carbon atoms in the isobutane and olefin reactants. The reaction, however, is a complex one, and besides the expected iso-paraffins, others of higher and lower carbon number are also produced.

It is generally accepted that alkylation proceeds through a carbonium ion

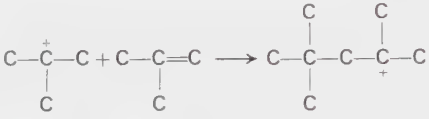
chain reaction, in which the tertiary butyl carbonium ion performs the chain carrying function. The initial carbonium ion may be generated by the addition of a proton (H^+) to an isobutene molecule in the presence of a strong acid (HF or H_2SO_4):

Initiation reaction



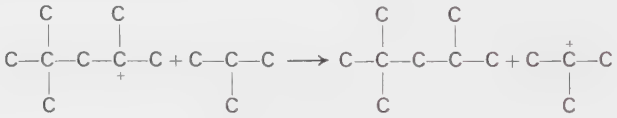
The t-butyl carbonium ion then reacts with a further olefin molecule (e.g. isobutene) as follows:

Addition reaction



On reaction with an isobutane molecule, the C_8 carbonium ion intermediate product is transformed into iso-octane (2,2,4-trimethylpentane):

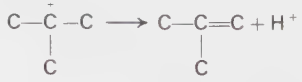
Propagation reaction



2,2,4-TMP

The chain of reactions will continue as the new t-butyl carbonium ion so formed is now free to undergo further olefin addition reactions as before. For example, it could combine with propene to form a C_7 carbonium ion, which will subsequently react with isobutane to produce iso-heptane (dimethylpentane). The reaction sequence is finally terminated when the t-butyl carbonium ion gives up its proton:

Termination reaction



Some of the secondary reactions which occur in alkylation are described as follows:

(a) *Isomerization.* With butene-1 and butene-2 reactants, isomerization to the more reactive isobutene form is believed to occur. Moreover, isomerization of the C_7 and C_8 carbonium ion intermediate products also takes place, so the final product of C_3 and C_4 alkylation in fact consists of a mixture of C_7 and C_8 isomers.

(b) *Hydrogen transfer.* When isobutane is alkylated with propene, hydrogen transfer reactions can result in the formation of propane and iso-octane. The final alkylate product thus contains a mixture of C_8, as well as the expected C_7 isomers. Similar hydrogen transfer reactions also occur when isobutane is alkylated with pentenes, giving a product containing isopentane and iso-octane.

(c) *Polymerization.* Further addition reactions between olefins and C_7 or C_8 carbonium ions can eventually result in the formation of small concentrations of higher boiling point isoparaffins, e.g. iso C_{10}–iso C_{12}.

(d) *Cracking.* A high carbon number carbonium ion, formed as an intermediate in polymerization reactions, may crack to a lower molecular weight carbonium ion plus an olefin. Both of these products are subject to further reaction under alkylation conditions and can account for many of the isoparaffins found in alkylate products.

(e) *Catalyst complexing.* Under unfavourable alkylation conditions, highly unsaturated complexes can form in the acid phase. These are known as 'acid soluble oils' in HF alkylation and as 'red oils' in sulphuric acid alkylation.

The alkylation process is exothermic, and the heat of reaction varies from 150 to 200 kcal/kg of alkylate product, depending on the olefin type. The formation of the more desirable C_7 and C_8 isoparaffins is favoured by low reaction temperatures, which are typically 10 °C for the sulphuric acid process and 35 °C with HF. Higher temperatures result in polymerization reactions, which increase the boiling range of the alkylate product and depress the octane number. The reaction is carried out at sufficient pressure to maintain the reactants in the liquid phase (10–17 bars).

Whether sulphuric acid or HF is used as catalyst, the alkylation process requires intimate mixing between the reactants and the acid phase. Moreover, very high concentrations of isobutane are essential to produce high quality alkylate and to minimize undesirable side reactions, such as polymerization and acid complex formation. Typically, the ratio of isobutane to olefin in the reactor charge is maintained between 8 and 15:1 by recycling excess isobutane back to feed.

Alkylate Yield and Quality

Under optimum conditions the alkylation process results in almost total conversion of olefins to alkylate product. Although a large excess of isobutane is required in the reaction zone, the actual consumption of isobutane per mole of olefin is only slightly higher than the stoichiometric ratio. The isobutane consumption for the various olefins used in the alkylation process is summarized in Table I, together with typical alkylate yields and octane numbers.

In terms of alkylate octane number, butenes are the most desirable olefin feedstock because the alkylate produced contains high concentrations of trimethylpentane isomers. One of these isomers, namely 2,2,4-trimethylpentane which is commonly referred to as iso-octane, is used as a reference fuel in the octane number test, and by definition has a research octane number

TABLE I
Typical Alkylate Yields and Properties

	Propene	Butenes	Pentenes
Yield, m^3 alkylate per m^3 olefin	1.76	1.77	1.7
Isobutane consumption, m^3 per m^3 olefin	1.31	1.15	1.0
Alkylate octane numbers:			
Research, unleaded	91	96	92
Motor, unleaded	89	94	90

(unleaded) of 100. The other reference fuel used in this test is n-heptane (not produced by alkylation) and this has a research octane number (unleaded) of zero.

Propene produces a slightly inferior alkylate due to the formation of the lower octane number dimethylpentanes (isoheptane isomers). Commonly, the mixed C_3–C_4 olefinic product from the catalytic cracker is fed to the alkylation unit and such an operation is summarized in Table II. It can be seen from the feedstock analysis that there is a deficiency in isobutane, which must be made up from other sources in the refinery, such as the catalytic reformer or hydrocracker.

Its high research octane number rating makes alkylate a valuable gasoline blending component, especially as environmental pressures are resulting in lead octane-enhancing additives being phased out of motor fuels. Of perhaps greater importance is its exceptionally high motor octane number, which can greatly offset the characteristically low motor octane ratings of the olefinic blending components, such as gasolines from the catalytic cracking unit. The research octane test measures the knock rating of a motor fuel at low engine speeds, whilst the motor octane method measures the high-speed knock characteristic. The difference between the research and motor octane numbers is often referred to as the 'sensitivity' of a gasoline, and the lower the sensitivity the more closely the actual performance of a fuel in a motor-car engine approaches its research octane number.

TABLE II
Alkylation with Mixed C_3–C_4 Feedstock

Olefin feed composition		Alkylate quality	
	% wt	Density, g/cc	0.699
		RVP, bar	0.4
Propene	22.8	ASTM distillation, °C	
Propane	11.2	10%	77
Isobutane	21.9	50%	102
n-Butane	9.9	70%	105
Butenes	32.8	90%	123
Isopentane	1.4	FBP	190
		Research octane (clear)	93.5
		Motor octane (clear)	91.5
Alkylate yield, m^3 per m^3 olefin		1.755	
Isobutane consumption, m^3 per m^3 olefin		1.175	

The alkylation process has many advantages over catalytic polymerization (see later) as a means of converting the light olefins from cracking units into a gasoline blending component. In addition to producing a much lower sensitivity gasoline, isobutane as well as olefins are converted, so the yield of gasoline is approximately doubled. Moreover, of these two processes, only alkylation can produce the high-performance gasoline required by supercharged aircraft piston engines.

Sulphuric Acid Alkylation

The major processes used in sulphuric acid alkylation are the Kellogg cascade autorefrigeration and the Stratford–Graham effluent refrigeration processes. Both are carried out at low temperatures in the range 3–12 °C, and as the names imply, refrigeration is employed to remove the exothermic reaction heat. Higher temperatures result in a significant decrease in alkylate quality as well as a large increase in acid consumption.

The high viscosity of sulphuric acid plus the large difference in density between the acid and the reactants, mean that vigorous mechanical agitation is required to achieve the desired degree of mixing between the two phases. Without good mixing, there is a tendency to promote polymerization reactions and to form acid complexes, which lead to a decline in alkylate quality and an increase in acid consumption.

A very simplified flow diagram for a typical sulphuric acid alkylation unit is shown in Fig. 1. The olefin feed, isobutane recycle and acid are contacted in the reaction system, and the heat of reaction is removed by low-temperature refrigeration. The hydrocarbon reactor effluent is treated to remove entrained acid materials and then fractionated in the de-isobutanizer to separate the

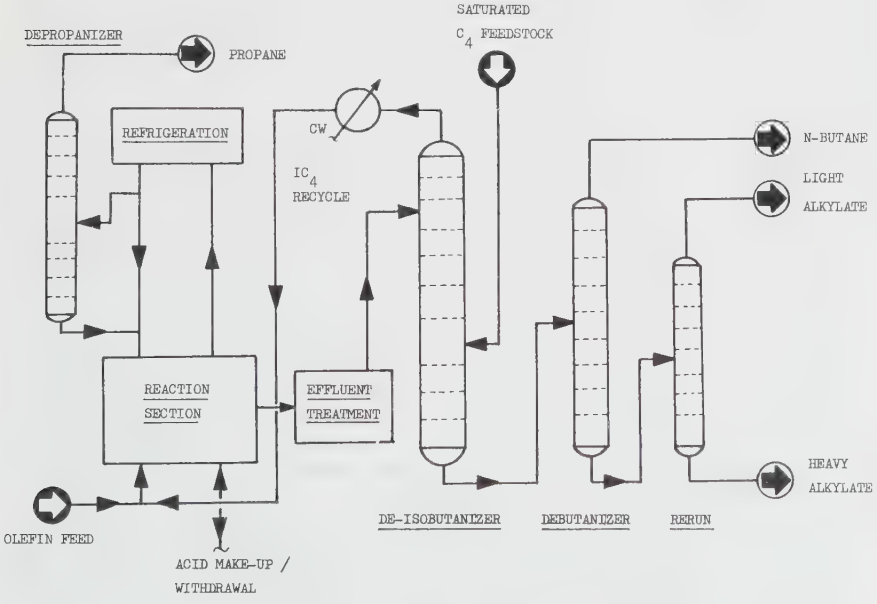


Fig. 1. Simplified sulphuric acid alkylation flow scheme.

isobutane recycle from the net products. Supplementary isobutane is provided by the saturated butane feedstock which is also fractionated in the de-isobutanizer. The de-isobutanizer bottoms product is subsequently de-butanized, and if required for aviation gasoline, the alkylate is split into light and heavy fractions on the re-run column.

Fresh 98–99 per cent sulphuric acid is added to the reaction section at the rate required to maintain the system acid at a strength of between 88 and 91 per cent, and spent acid is withdrawn from the process to control system inventory. The lower limit of system acid strength is dictated by the danger of dropping into a region of excessive polymerization and ester formation, whilst the upper limit is dictated by the economics of acid consumption and octane requirement.

Acid consumption with the sulphuric acid process is strongly dependent on the type of olefin feedstock and the contaminant levels. With butene feedstocks, acid consumptions vary between 35 and 60 kg per m^3 alkylate, but this is very much influenced by traces of butadiene, which are always present in cracker C_4 streams. For example, the C_4 product from a modern fluid catalytic cracking unit contains about 0.3% mol butadiene. Diolefins react with concentrated sulphuric acid to form tars, SO_2, CO_2, and water, and it has been estimated that 1 kg of butadiene in alkylation feedstock will result in about 10 kg of 98 per cent sulphuric acid being degraded to a strength of 90 per cent.

Due to its tendency to produce esters (e.g. isopropyl sulphate), propene alkylation results in very much higher acid consumption than with butene feedstocks, and this could typically be 100–150 kg acid per m^3 alkylate. For pentene feedstocks, acid consumptions 1.3–1.5 times greater than for butenes have been reported.

It is thus apparent that the quantity of fresh acid required by the sulphuric acid alkylation process can be very considerable. For example, for a plant producing 500 m^3/day of alkylate from the mixed C_3 C_4 feedstock described in Table II, a fresh acid consumption of about 40 t/day would be expected. A similar quantity of spent acid would require disposal to a neighbouring sulphuric acid recovery facility.

Feedstock to the alkylation unit is normally treated by alkanolamine and caustic extraction to remove H_2S and mercaptan sulphur, both of which can adversely affect acid consumption. After such treatment, the feed is saturated with dissolved water (about 500 ppm) and this undoubtedly also contributes towards high acid consumptions. However, it has generally not been considered economic to install feedstock driers.

In sulphuric acid alkylation, corrosion is not normally a severe problem. Carbon steel is resistant to sulphuric acid of the strength used, and is used for the construction of reactors, vessels, and associated piping. Some side reactions, however, result in the formation of sulphur dioxide, and, in the presence of water which enters the unit with the feedstock, this can give rise to acid corrosion in the depropanizer overheads system. Furthermore, both acidic and neutral esters entrained with the reactor effluent, if not removed, can give rise to corrosion problems due to decomposition in the downstream fractionators. Effluent treatment normally consists of caustic washing to remove the acidic material, while neutral esters can be hydrolysed by washing the effluent with hot water at about 65°C.

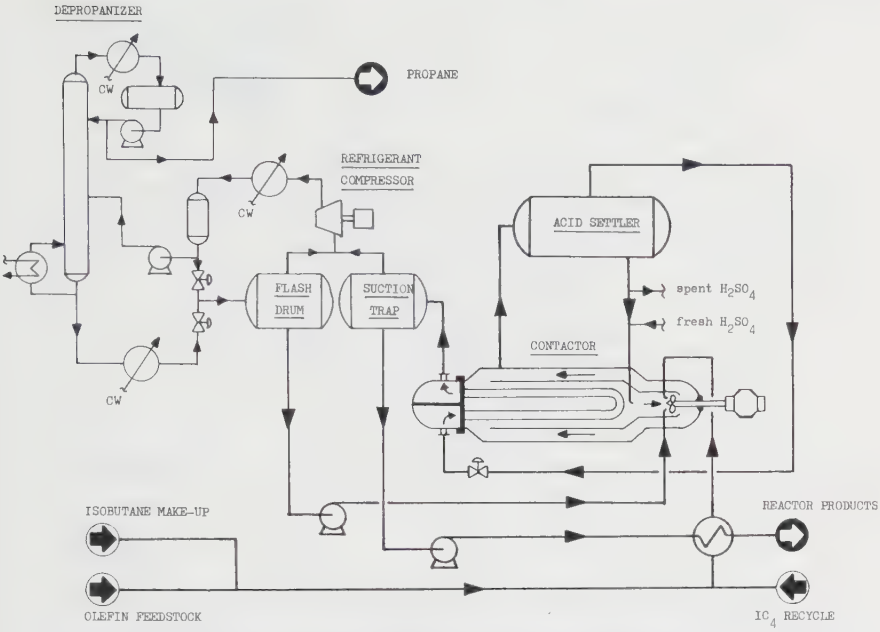


FIG. 2. Stratford–Graham effluent refrigeration alkylation process.

(*a*) *Stratford–Graham process*

The Stratford Graham effluent refrigeration alkylation process is shown diagrammatically in Fig. 2. The heart of the process is the reactor or contactor, within which the acid and hydrocarbon reactants are circulated at high velocities by means of an internal axial flow impeller. The entire volume of liquid in the contactor is maintained at a uniformly low temperature by means of the reactor effluent, which acts as a refrigerant when allowed to partially vaporize through the contactor tubes.

On leaving the contactor tubes, the reactor effluent passes to the compressor suction trap for vapour/liquid separation, and the vapour is then sent to the compressor before being liquefied. The liquid so produced is split into two streams, one of which passes to the depropanizer, whilst the other is sent to a low pressure flash drum where partial vaporization again causes the temperature to fall. Cold liquid from the flash drum is then pumped to the contactor to provide additional cooling.

(*b*) *Kellogg cascade process*

The Kellogg cascade autorefrigeration process shown in Fig. 3 differs from the Stratford Graham process in that refrigeration is provided *in situ* by allowing a proportion of the reactants to vaporize within the reaction zone.

In the cascade system, dilute olefin concentrations are achieved by splitting the olefin feed into a number of parallel streams, each of which is fed to a separate reaction compartment containing its own mixer. The required low

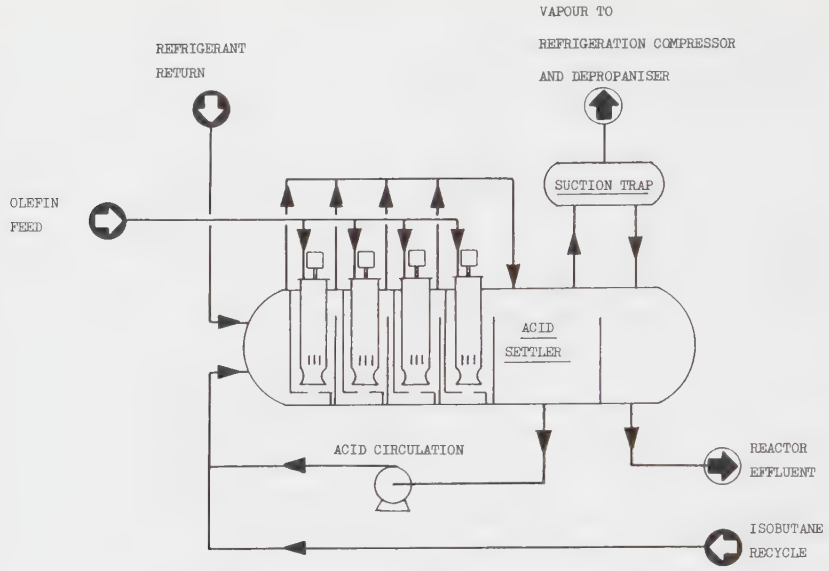


FIG. 3. Kellogg cascade autorefrigeration alkylation process.

temperature is maintained by allowing vaporization in each compartment to remove the heat of reaction. Reactor vapours are sent to the compressor and then liquefied before being split into two streams. Part of the liquid refrigerant passes to the depropanizer for propane removal, whilst the remainder combines with the depropanizer bottoms stream and is sent to a low pressure flash drum. Here, partial vaporization causes the temperature to fall once again and the cold liquid remaining is sent back to the reaction zone to provide additional cooling.

Acid collects in a settling zone before being recirculated back to the reactor feed, whilst the liquid hydrocarbon reactor effluent flows over a weir into a compartment at the end of the reactor vessel before passing to the treatment and fractionation sections of the unit.

Hydrogen Fluoride Alkylation

Although the majority of early alkylation units used sulphuric acid as catalyst, there has been a strong trend over recent years in favour of the HF process. Today, the installed capacity of each process is roughly comparable. The reason for this trend is not clear, but is probably due mainly to the cost and environmental implications of sulphuric acid supply and disposal.

The HF alkylation process is offered by two licensors, namely Universal Oil Products and Phillips Petroleum, and a simplified flow diagram representing both is shown in Fig. 4. The reaction is carried out at temperatures between 25 and 45 °C, which are considerably higher than with the sulphuric acid process. Hence, cooling water can be used to remove the heat of reaction, rather than the more expensive refrigeration system. However, a consequence of the higher reaction temperature is a somewhat lower alkylate octane number. In some

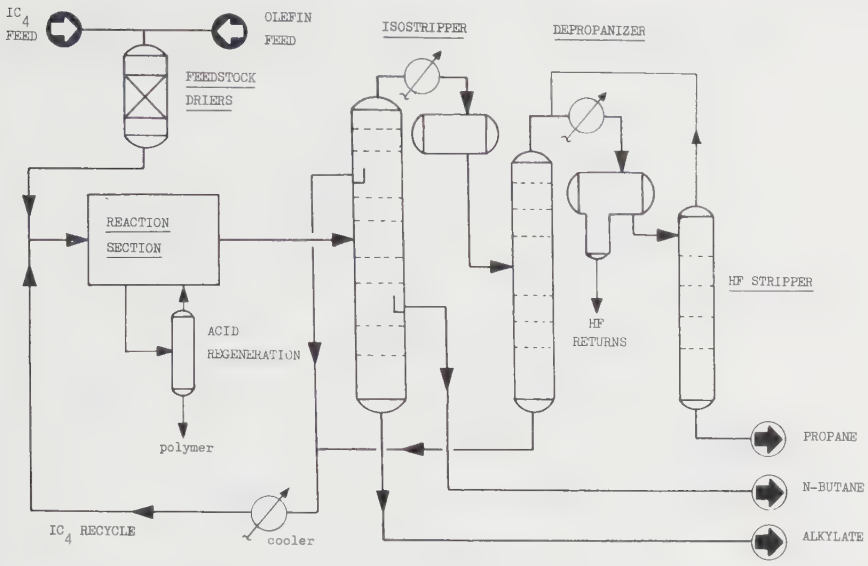


FIG. 4. Simplified hydrogen fluoride alkylation flow scheme.

cases this can mean that the HF process is not suitable for producing high-performance aviation gasolines, but for most purposes product quality is highly satisfactory.

Hydrogen fluoride is a volatile liquid boiling at 19°C, has a density of 1.0 g/cc at 15°C, is chemically very stable, and can be distilled unchanged under the conditions employed for fractionating light hydrocarbons. Due to its very low viscosity, HF requires very much less energy than sulphuric acid to achieve the required degree of mixing in the reaction zone. In the anhydrous state, or containing up to 2 per cent dissolved water, HF can be handled satisfactorily in carbon steel equipment, but corrosion increases rapidly at higher water contents. Feedstocks must therefore be thoroughly dried over activated alumina or molecular sieves before entering the reaction section. In spite of the corrosion aspects, some water in the HF is believed to be necessary to suppress undesirable polymerization reactions which can adversely affect alkylate quality.

Products from the reaction zone pass to the de-isobutanizer column (commonly referred to as the Isostripper), from which alkylate is withdrawn as a bottoms product. N-butane, which passes through the alkylation unit unchanged, is removed as a side-cut, while propane and a portion of the isobutane pass overhead. The main flow of isobutane recycle is withdrawn as an upper side-cut before being cooled and returned to the reactor feed.

The Isostripper overheads stream passes first to a depropanizer, where the remainder of the isobutane recycle is taken as a bottoms product, and dissolved HF is then removed from the propane product in the HF stripper. It should be remembered that the hydrocarbon reactor effluent contains about 1–2 per cent dissolved HF, and this is eventually recovered in the Isostripper and depropanizer overheads receivers before being returned to the reaction system.

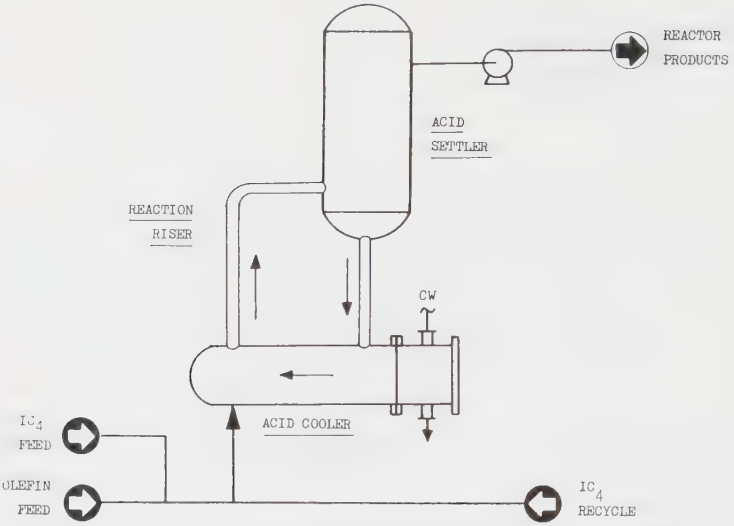


FIG. 5. Phillips HF alkylation process.

Acid strength is maintained at about 85–90 per cent by withdrawing a slip-stream to the HF re-run tower where acid-soluble oils are removed as a bottoms product. This *in situ* acid regeneration facility means that the net acid consumption with HF alkylation is considerably lower than with the sulphuric acid process. Typical acid consumptions vary between 0.3 and 0.5 kg per m^3 alkylate, this being partly due to the formation of inert organic fluorides which leave the unit with the C_3, C_4, and alkylate products. As with sulphuric acid alkylation, sulphur compounds must be removed from the feedstock to minimize acid consumption.

(*a*) *Phillips HF alkylation*

The Phillips HF alkylation process is represented diagrammatically in Fig. 5. The reactor/settler design uses the principle of differential gravity head to effect high acid circulation rates through a cooler prior to contacting the HF with highly dispersed hydrocarbon in the reaction riser. Hydrocarbon feedstock plus isobutane recycle are introduced at high velocity at the base of the reaction riser. Liquid HF catalyst is entrained at this point and the mixture of hydrocarbons and HF passes up the riser into the acid settler. The HF rapidly separates from the hydrocarbon phase and is then returned by gravity to the acid cooler where the exothermic heat of reaction is removed.

(*b*) *UOP HF alkylation process*

The Universal Oil Products HF alkylation process, shown in Fig. 6, differs from the Phillips process in that the hydrocarbon reactants, as well as the acid, flow through the cooler. The cooler (reactor) effluent passes to an acid settler where separation of the two phases takes place, and acid is then recycled back to the reactor, usually with the aid of a large centrifugal pump.

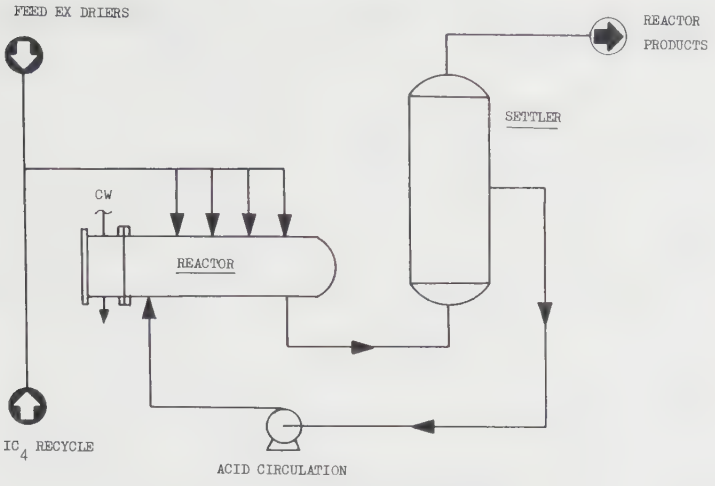


FIG. 6. UOP HF alkylation process.

ISOMERIZATION

Paraffin Isomerization

The importance of isomerization in petroleum refining operations is twofold. First, it is valuable for converting n-butane to isobutane, which may then be alkylated to liquid hydrocarbons in the motor gasoline boiling range. Secondly, it can be used to increase the octane number of the paraffins boiling in the gasoline boiling range by converting some of the n-paraffins into the more desirable isoparaffins.

The isomerization reaction is a reversible first-order reaction limited by thermodynamic equilibria. The reaction is mildly exothermic and does not occur significantly without the aid of a catalyst. The thermodynamic equilibria for pentanes and hexanes shown in Fig. 7 indicate that low reaction temperatures favour production of the more desirable isomers.

Basically, the process involves contacting hydrocarbon and catalyst under conditions which give favourable equilibria and a good reaction rate. Originally, the choice of catalyst was between aluminium chloride promoted with hydrochloric acid and a platinum-containing catalyst, the latter operating at higher temperatures. In the late 1960s modified platinum-containing catalysts were developed capable of giving the required reaction rates at lower temperatures. Aluminium chloride sublimes at reaction temperatures and is sufficiently soluble when operating under liquid phase conditions to be carried from the reactor, causing plugging and failure of the product recovery system. Hence the development of the new platinum catalysts assisted in producing a more easily operable process.

Butane Isomerization

Two processes are primarily in use, namely the UOP butamer process and the BP butane isomerization process. A flow diagram of the butamer process is shown in Fig. 8.

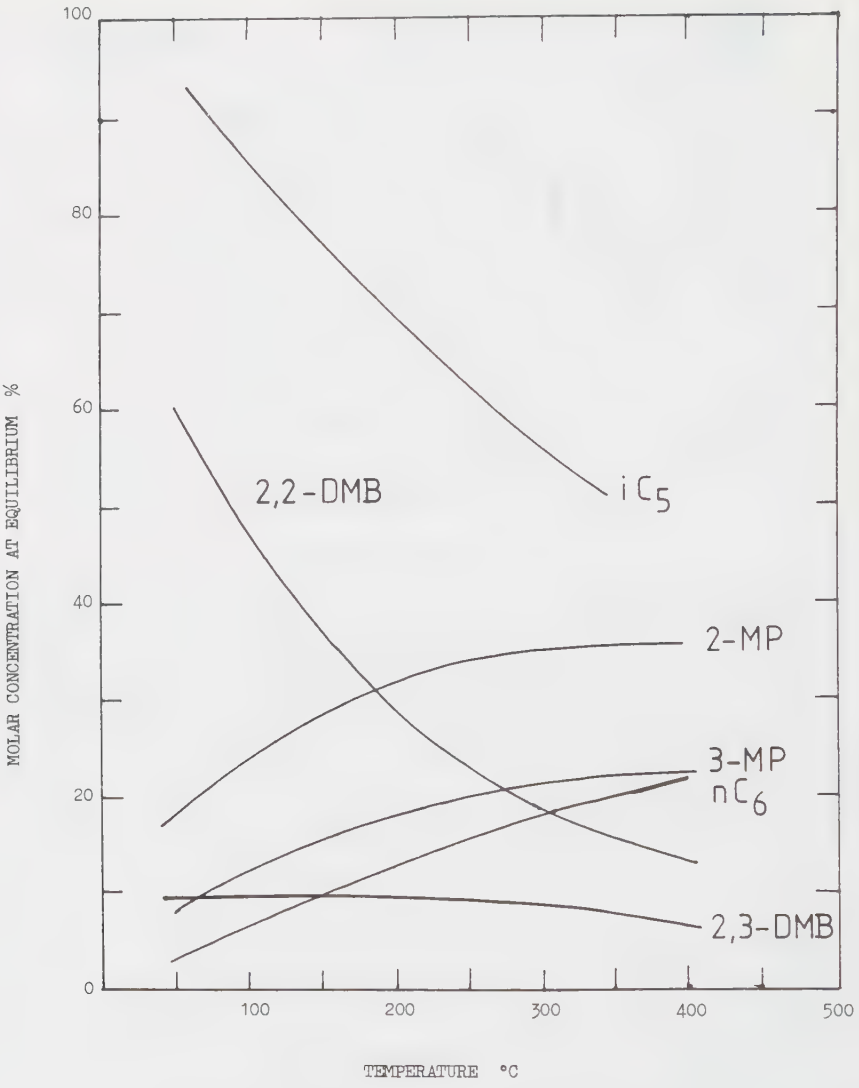


FIG. 7. Thermodynamic equilibria for pentanes and hexanes.

The mixed butane feed is fed to a distillation column to separate isobutane from n-butane. The n-butane feed to the process is taken from the base of the column, mixed with a hydrogen-rich recycle gas, heated to reaction temperature, and then passed to the reactor containing a platinum catalyst. The n-butane is isomerized to a near-equilibrium concentration of isobutane and then passes to a separation vessel. The recycle gas is separated from the butane product, then mixed with a small quantity of hydrogen-rich make-up gas and returned to the process. The butane product passes to a stabilization column to remove dissolved gas and breakdown products, and is then sent back

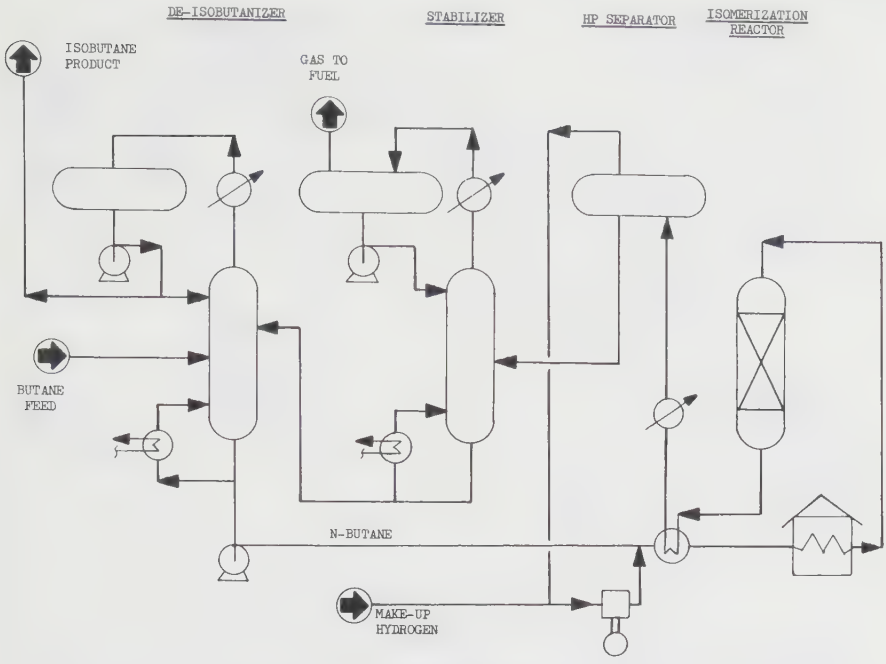


FIG. 8. UOP butamer isomerization process.

to the butane splitter column where the desired isobutane product is taken off as an overheads stream. The unconverted butane, together with fresh n-butane in the feed, is returned to the process.

The BP process is similar, differing mainly in the type of catalyst used.

Pentane and Hexane Isomerization

Isomerization of pentanes and hexanes has become more widespread in recent years with the reduction of lead alkyls permitted in motor gasoline. C_5 and C_6 isoparaffins provide excellent high-octane components in the lower boiling end of the gasoline, which is often deficient in high-octane components, particularly with gasolines of high octane number produced by catalytic reforming. The octane numbers of the normal and isoparaffins are compared in Table III.

The process flow diagram is similar to that for butane isomerization for once-through operation, although the BP process for C_5/C_6 or C_6 isomerization has two isomerization reactors (Fig. 9).

The process can produce a product of 86.5 RON from a pentane feedstock, 81.0 RON from hexanes and a 84.5 RON product from a mixed pentane/hexane feedstock. Typical once-through product compositions with C_5 and $C_{5/6}$ feedstocks are shown in Table IV.

As isomerization processes produce near-equilibrium mixtures of isomers, they lend themselves to be combined with various physical separation processes, such as distillation or molecular sieve extraction to give near-quantitative

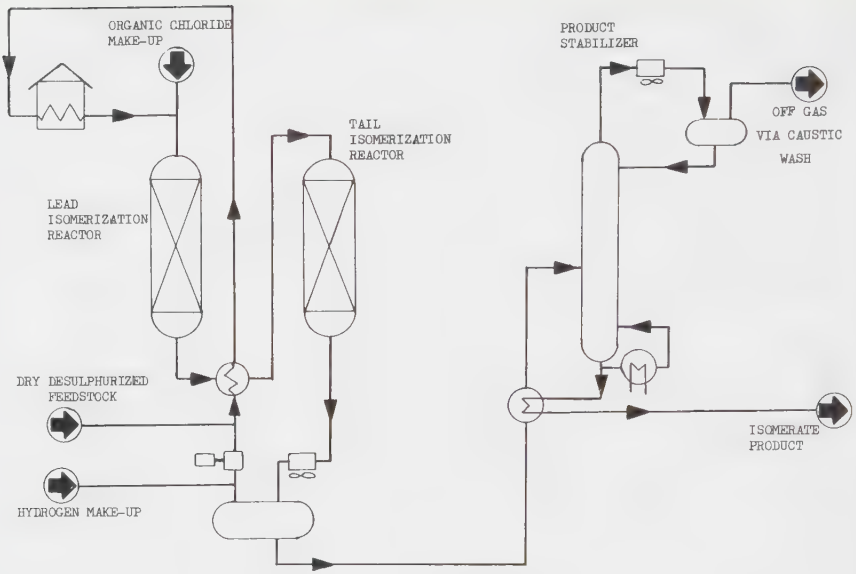


FIG. 9. BP C_5/C_6 isomerization process.

conversions to the higher octane number materials—isopentane and/or selected C_6 isomers. Products having octane numbers as high as 92 can be produced, depending on the sophistication of the equipment used.

Three commercial processes are available, namely the Shell/Union Carbide Total Isomerization Process, UOP Penex, and the BP Process as already mentioned. The Shell/Union Carbide process differs from the other two in aiming for a lower conversion in the isomerization reactor (Shell Hysomer process), and incorporates molecular sieve technology (Union Carbide) to separate the normal paraffins from the isomerization reactor product. A simplified flow diagram is shown in Fig. 10. It is claimed that optimum isomerization performance can be obtained with feedstocks containing up to

TABLE III

Boiling Points and Octane Numbers of Pentanes and Hexanes

Compound	Boiling point (°C)	Octane number	
		Clear	+3 ml TEL/US Gal
n-Pentane	36	61.7	84.7
Isopentane	28	92.6	103.5
n-Hexane	69	34.0	65.3
2-Methylpentane	60	73.4	92.2
3-Methylpentane	63	74.5	92.3
2,2-Dimethylbutane	50	92.3	103.4
2,3-Dimethylbutane	58	103.5	112.0
Cyclopentane	49	101.3	111.1

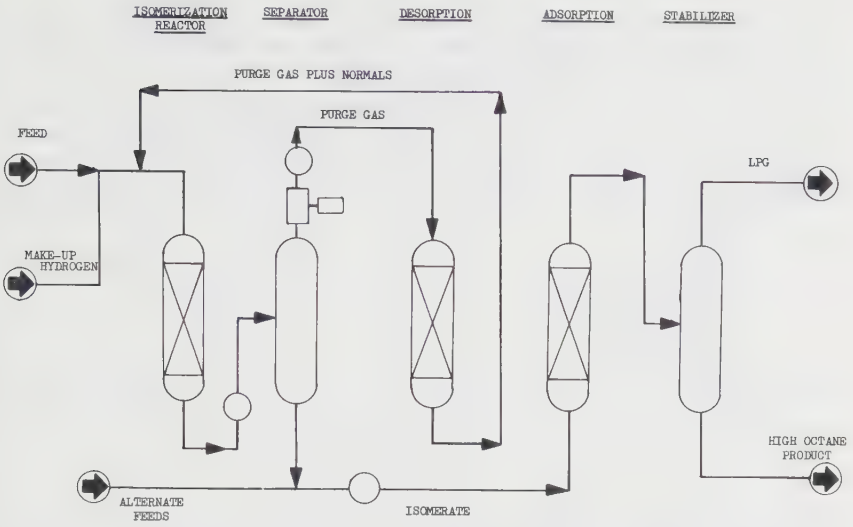


FIG. 10. Shell/Union Carbide total isomerization process.

10 ppm sulphur and 30 ppm water. The catalyst in the Shell Hysomer reactor differs from the other two processes as it uses a noble metal on a zeolite base. Typical product compositions from the TIP process are given in Table V.

The BP and UOP processes may also be designed to incorporate molecular sieve technology, but this is not normally included as part of the design package.

The BP process is claimed to be the only one with a regenerable catalyst system. The catalyst is charged to the isomerization unit reactors as a non-corrosive platinum-on-alumina material. The active catalyst is generated *in situ*

TABLE IV
BP Isomerization Process: Typical Stream Compositions

	C_5		$C_{5/6}$	
Feedstock	Feed	Product	Feed	Product
Component, % wt				
C_4 and lighter	—	—	0.2	1.1
Isopentane	2.6	77.6	24.6	39.7
n-Pentane	95.9	21.2	26.8	11.8
Cyclopentane	1.5	0.4	1.7	1.3
2,2-Dimethylbutane	—	0.7	1.0	16.0
2,3-Dimethylbutane	—	0.1	2.9	4.4
2-Methylpentane	—	—	15.0	12.3
3-Methylpentane	—	—	11.3	6.8
n-Hexane	—	—	13.1	4.2
Benzene	—	—	1.7	—
Methylcyclopentane	—	—	1.7	1.3
Cyclohexane	—	—	—	1.1
RON-Clear	63.1	86.6	72.2	84.6

TABLE V
Shell Union Carbide TIP Process: Typical Stream Compositions

	Feed C_5/C_6	Hysomer product	TIP product
Component, % wt			
Butanes	0.7	1.8	2.8
Isopentane	29.3	49.6	72.0
n-Pentane	44.6	25.1	2.0
2,2-Dimethylbutane	0.6	5.0	5.5
2,3-Dimethylbutane	1.8	2.2	2.5
Methylpentanes	13.9	11.3	13.4
n-Hexane	6.7	2.9	<0.1
Cyclic C_5 C_6	2.4	2.1	1.8
RON-Clear	73.2	82.1	90.7

by means of an organic chloride compound. Thus, at the end of a process cycle the coked catalyst can be regenerated in a manner similar to reforming catalysts, and then reactivated in the same way as fresh catalyst.

Aromatic Isomerization

Aromatic isomerization is practised mainly with mixtures of C_8 aromatics to maximize the production of para and ortho xylenes. The process is frequently found in the petroleum refinery, taking a selected cut from catalytic reforming operations. The products are primarily for use in the chemicals industry and this application is discussed in more detail in another chapter.

CATALYTIC POLYMERIZATION

In an oil refinery, this process is used to convert light olefins, such as propene and butenes, into a high octane number motor gasoline component.

Catalytic polymerization was first developed in the 1930s for converting the olefinic off-gases from thermal cracking into motor fuel, and was soon afterwards extended to the processing of light ends from the catalytic cracking process. Although to some extent superseded by alkylation, catalytic polymerization still plays an important role in today's refining industry.

Catalytic polymerization also finds application in the petrochemicals industry for producing straight chain C_7–C_9 olefins, which are used in the manufacture of speciality alcohols. This process can also be used for the alkylation of aromatics with olefins to form products such as cumene and ethylbenzene, which are intermediates in the manufacture of phenol and styrene.

The popular name for this process is really a misnomer, since the product consists mainly of dimer and trimer, with increasingly smaller amounts of tetramer and higher boiling oligomers. Although the name 'catalytic condensation' is perhaps a more accurate description, this process is still commonly referred to as 'polymerization'.

The current catalytic polymerization process is based almost entirely on the

use of a solid catalyst consisting of phosphoric acid supported on an inert porous material such as kieselguhr. Earlier processes using catalysts such as sulphuric acid or phosphoric acid, either in the liquid phase or in the form of copper pyrophosphate, are of little importance today.

It is believed that catalytic polymerization proceeds through the formation of carbonium ions, which are the result of the reaction between an olefin and a strong acid. A suggested reaction scheme for the dimerization of propene is as follows:

$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + H^+ \xrightarrow{\text{Strong acid}} \underset{\text{Carbonium ion}}{CH_3{-}\overset{+}{C}H{-}CH_3}$$

The carbonium ion so formed is highly reactive and rapidly combines with a second propene molecule to produce a new carbonium ion.

$$CH_3{-}\dot{C}H + CH_2{=}CH{-}CH_3 \longrightarrow CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}\dot{C}H{-}CH_3$$

The proton originally donated to the initial propene molecule is then released to form a C_6 olefin.

$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}\dot{C}H{-}CH_3 \longrightarrow \begin{cases} CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH{=}CH_2 + H^+ \\ CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}CH{=}CH_2 + H^+ \end{cases}$$

Butenes and mixtures of propene and butenes react in a similar manner to form C_7 and C_8 olefins. Further addition reactions may also occur in which C_9, C_{12}, C_{16}, etc. olefins are formed, but for gasoline production, plant design and operating conditions are normally set to minimize the production of such higher boiling point material.

Of the butenes, isobutene is the most reactive due to the relative ease with which tertiary carbonium ions are formed. If the process is operated at relatively low reactor temperatures (150°C), isobutene can be selectively polymerized to form a product containing highly branched chain C_8 olefins. This material can then be hydrotreated to produce a high-quality motor fuel containing a significant proportion of 2,2,4-trimethylpentane (iso-octane) which is suitable for use as aviation gasoline. It is doubtful, however, whether this processing route would be as economic as alkylation.

Somewhat higher temperatures (about 200°C) are required to polymerize the remaining butene isomers (butene-1 and butene-2) and propene. Although some isomerization reactions may also occur, butene-1 tends to produce a more linear product than the other butene isomers, and such material can subsequently be used in the manufacture of plasticizer alcohols.

Early polymerization processes were carried out at low pressures with the hydrocarbon feedstock in the vapour phase. These suffered from the disadvantage that the catalyst surface would tend to become coated with high

boiling polymers, which then proceeded to form coke. Frequent catalyst regeneration was consequently required to maintain an acceptable level of activity, and hence conversion.

The modern process takes place at much higher pressures (35–70 bars) such that the reaction occurs entirely in the liquid phase. This results in the heavier polymer being washed from the surface of the catalyst, thereby greatly reducing the rate of de-activation and eliminating the need for regeneration.

Feedstock to a catalytic polymerization unit frequently consists of the C_3–C_4 produced from a catalytic cracker. This material is rich in olefins and contains about 70 per cent propene in the C_3 fraction, whilst the C_4 fraction contains about 55 per cent butenes. A typical composition is given in Table VI.

TABLE VI
Composition of Catalytic Cracker C_3–C_4

Component	% mol
Ethane	0.8
Propane	11.3
Propene	26.2
Isobutane	20.9
n-Butane	6.4
Isobutene Butene-1 Butene-2	33.4
C_5 and heavier	1.0

Other feedstocks may include the olefinic C_3–C_4 products from thermal cracking operations such as visbreaking and coking, or from steam cracking.

Impurities such as sulphur compounds and ammonia are present in some of these streams, and these must first be removed. This is commonly carried out by washing the feedstock with an alkanolamine solution to remove hydrogen sulphide, followed by caustic washing to remove mercaptans. Sulphur compounds in the feed are undesirable for a number of reasons. First, they result in the formation of higher boiling sulphur compounds in the gasoline product, which give rise to an unacceptably foul odour. Secondly, they lead to a more highly coloured product which requires re-distillation before it can be used in motor gasoline. However, there is no evidence to suggest that sulphur is a poison for the solid phosphoric acid catalysts currently in use.

A final water wash removes traces of ammonia and other basic compounds which would otherwise neutralize catalyst acidity and result in rapid loss of activity.

UOP Catalytic Polymerization Process

A typical flow scheme for a UOP catalyst polymerization unit with a chamber-type reactor is shown in Fig. 11.

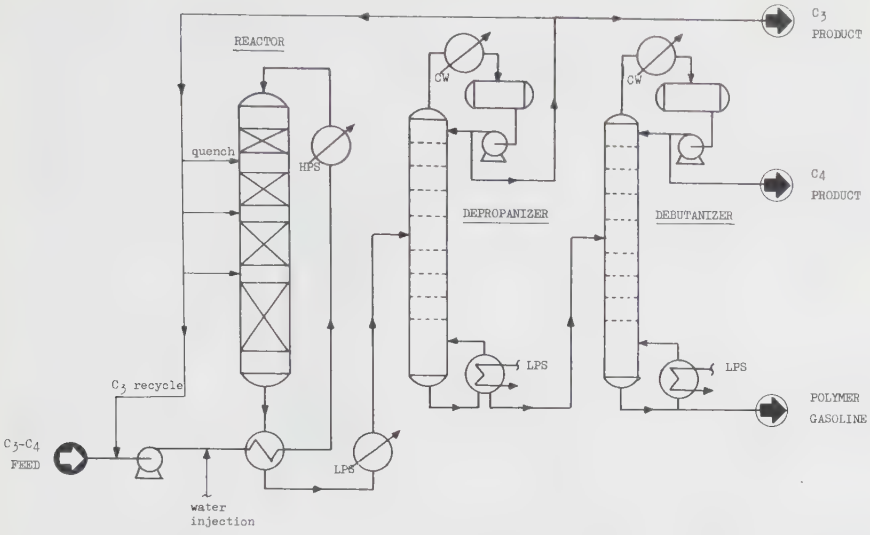


FIG. 11. UOP catalytic polymerization unit with chamber reactor.

The catalytic polymerization reaction is exothermic, releasing about 370 kcal/kg and 220 kcal/kg of olefin converted for propane and butene, respectively. To control reaction temperatures in this design, the catalyst is arranged in a series of separate beds to allow the injection of cold recycle propane as quench. Without correct temperature control, excessive polymerization to undesirable high boiling point products and coke formation would result. Moreover, to control the temperature rise across each bed, propane is recycled back to feed to limit the olefin content of the reactor charge to about 30% vol (max).

Although the reactor feed contains dissolved water from the pretreatment washeries, additional water must be injected to maintain the correct degree of hydration on the phosphoric acid catalyst. Control of water injection is of great importance, since an under-hydrated catalyst will promote heavy polymer and coke formation, whilst over-hydration results in softening of the catalyst, often to the point of plugging the reactor.

Reactor effluent, after heat exchange with feed, passes to the depropanizer and debutanizer columns, where saturated propane and butane, plus any unconverted olefins, are removed from the polymer gasoline product.

The alternative UOP tubular reactor design is shown in Fig. 12. In this case, the catalyst is contained in a large number of 2-inch vertical tubes surrounded by a water jacket to remove the exothermic heat of reaction. The steam generated in the water jacket is then used to preheat the feed.

This design can accept reactor feedstocks containing up to 50% mol olefins with C_4 and mixed C_3-C_4 streams, but with C_3 feedstocks olefin contents are restricted to 45% mol because of the higher heat of reaction. The quantity of recycle required by the tubular reactor system is substantially lower than with the chamber reactor, and thus the energy consumed in producing the recycle material is greatly reduced. In general, the exothermic heat of reaction is

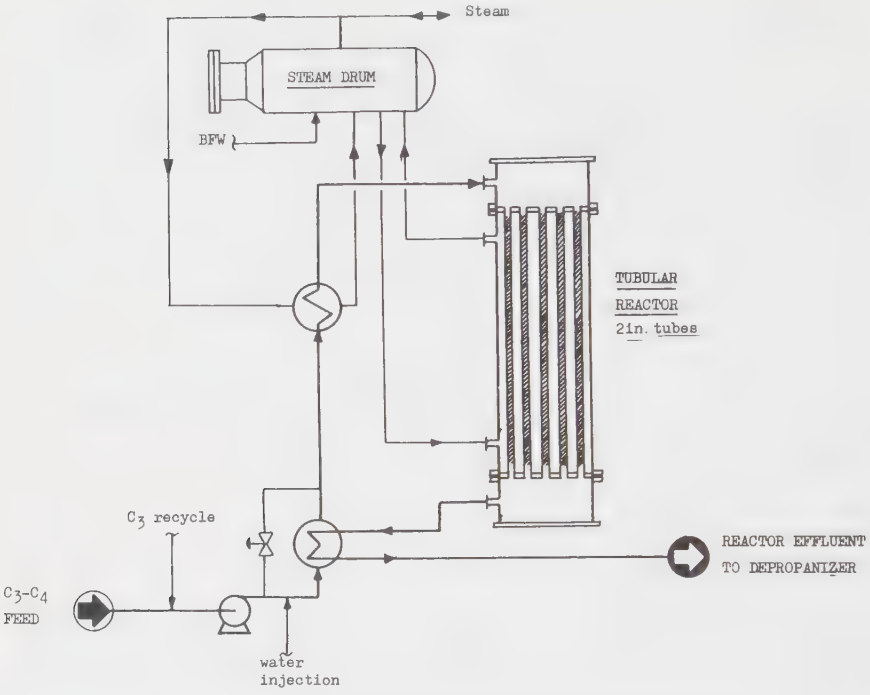


FIG. 12. Tubular catalytic polymerization reactor arrangement.

TABLE VII

Catalytic Polymerization Yields and Product Qualities

Mixed C_3–C_4 feedstock:	
Propene, % wt	21.4
Butene, % wt	36.3
Yields, % wt	
Propane	12.8
Butane	34.3
Polymer gasoline	52.9
Polymer gasoline quality:	
Density at 15 °C, g/cc	0.735
Research octane (unleaded)	95.5
Motor octane (unleaded)	82.0
Distillation, °C	
10%	102
50%	120
90%	175
FBP	220
C_6 olefins, % wt	4.6
C_7 olefins, % wt	45.3
C_8 olefins, % wt	25.3
C_9 olefins, % wt	16.6
C_{10+} olefins, % wt	10.0

theoretically sufficient to maintain the tubular reactor system in heat balance, provided the feedstock olefin content exceeds 28% mol.

Whichever reactor design is adopted, the catalytic polymerization process achieves olefin conversions of 85 95 per cent, depending on feedstock quality, operating conditions, and catalyst activity. Typical yields and product qualities are summarized in Table VII. Although the polymer gasoline has a relatively high research octane number (low-speed knock characteristic), the motor octane number (high-speed knock characteristic) is poor due to its highly olefinic nature.

IFP Dimersol Process

The IFP Dimersol process is a once-through process which dimerizes propene to a high octane number hexene motor gasoline blending component. The process can also be used for co-dimerizing propene and butene, or for dimerizing butene, to provide linear C_7 and C_8 olefins for speciality alcohols manufacture.

Dimersol makes use of a homogeneous liquid-phase catalyst system comprising a nickel co-ordination complex and an aluminium-alkyl, which are continuously injected in small concentrations into the feedstock. The flow scheme for a C_3 Dimersol unit is shown in Fig. 13.

The reaction takes place at ambient temperature with sufficient pressure to maintain the feedstock in the liquid phase, and reactor temperature is carefully controlled by removing the exothermic heat of reaction in the recycle cooler.

The catalyst is destroyed immediately on leaving the reactor by injection of a

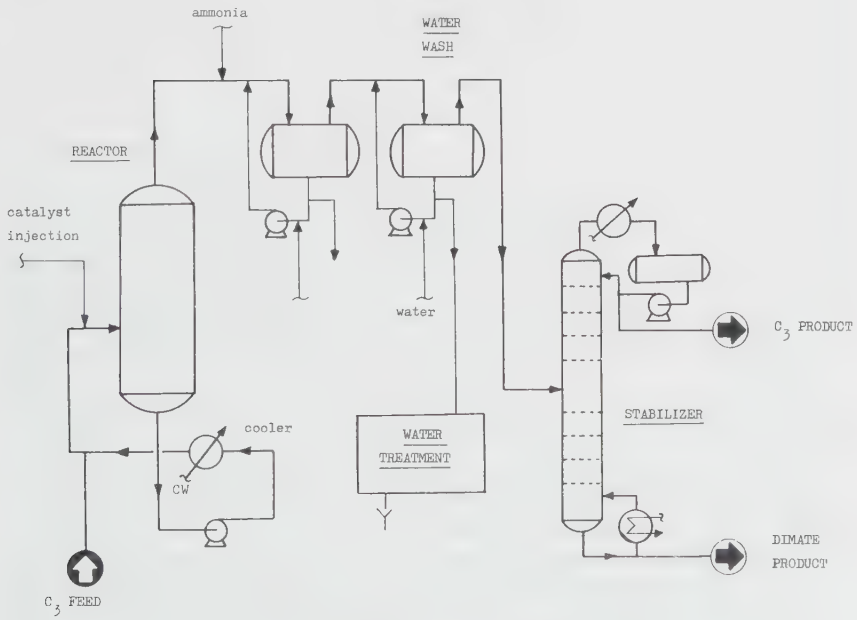


Fig. 13. IFP Dimersol process.

stream of ammonia, and the product is then water washed to extract inorganic material. The reactor effluent is finally sent to the stabilizer to separate a C_3 LPG stream from the dimate product.

Unlike catalytic polymerization with phosphoric acid, the Dimersol catalyst system is believed to be very sensitive to feedstock impurities such as water, sulphur, ammonia, diolefins, and acetylenes. More extensive feedstock treatment, including drying over molecular sieves, is therefore necessary. The process is unsuitable for feedstocks containing significant concentrations of isobutene, and so cannot be used for C_4 or mixed C_3–C_4 streams from catalytic cracking units.

Table VIII gives a typical inspection analysis for a C_3 dimate product. The main advantage of Dimersol over C_3 polymerization with phosphoric acid is

TABLE VIII
Inspection Analysis of C_3 Dimate

Density at 15°C, g/cc	0.686
Research octane (unleaded)	96.5
Motor octane (unleaded)	82.0
Distillation, °C	
10%	68
50%	73
90%	134
FBP	196

that the selectivity to hexene is greatly enhanced. Whereas catalytic polymerization produces significant quantities of trimer and tetramer, Dimersol is reported to give a product containing 80 85% wt hexene. This results in a lower density, lower boiling point product which is a more desirable component in the final motor gasoline blend.

HYDROTREATMENT

Rapid increases in catalytic reforming capacity have created large volumes of valuable by-product gas containing hydrogen in a reasonable concentration. This fact has led to a marked increase in catalytic desulphurization and other hydrogen-consuming processes. Over the last decade the need for more desulphurization capacity has arisen, due to increased environmental pressures requiring less pollution of the atmosphere with sulphur and nitrogen compounds.

Catalytic desulphurization is used now to desulphurize fractions right across the whole crude boiling range. These include:

(a) Naphtha desulphurization prior to catalytic reforming;
(b) Desulphurization of kerosines and diesel oils to lower sulphur levels to reduce atmospheric pollution;
(c) Desulphurization of vacuum distillates to reduce the sulphur content of catalytic cracker feedstocks, thereby reducing sulphur dioxide emissions; and
(d) Desulphurization of residues to reduce the sulphur content of fuel oils.

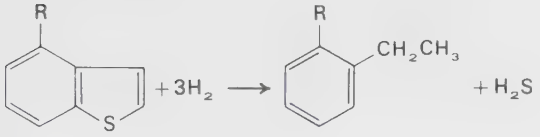
Catalytic desulphurization is known under a variety of names, e.g. hydrodesulphurization, hydrotreating, and hydrofining, and also under proprietary names such as Unifining, Hydrobon, H-Oil, etc.

The main reaction in catalytic desulphurization processes is the elimination of sulphur in the form of hydrogen sulphide. The following reactions with mercaptans, sulphides, disulphides, thiophenes, and benzothiophenes exemplify the most common reactions:

$$RSH + H_2 \longrightarrow RH + H_2S$$

$$R_1SR_2 + 2H_2 \longrightarrow R_1H + R_2H + H_2S$$

$$R_1SSR_2 + 3H_2 \longrightarrow R_1H + R_2H + 2H_2S$$



The extent of sulphur removal can be controlled by the choice of operating conditions, and levels up to 99 per cent and greater can be obtained. The hydrocarbons formed as a result of the desulphurization reactions boil at temperatures appreciably lower than those of the original sulphur compounds. Thus, when appreciable quantities of sulphur are removed, relatively large quantities of lower boiling hydrocarbons will be produced, which will require the product to be stripped to preserve flash point and boiling range specifications.

The fact that the sulphur is removed as hydrogen sulphide is an advantage, since the hydrogen sulphide may be extracted easily from the sour gas product. Many different absorbents are used, including MEA, DEA, and DIPA. The pure hydrogen sulphide produced is then sent to a sulphur recovery plant (see later section) for the manufacture of sulphur to a high degree of purity.

The catalyst and process conditions are normally chosen to minimize any side reactions such as dehydrogenation, hydrocracking, and aromatic saturation. Oxygen and nitrogen compounds may be converted to water and ammonia, respectively, depending on the catalyst and operating conditions used, and in the heavier fractions, such as atmospheric and vacuum residues, removal of metal compounds also takes place.

Catalysts used for desulphurization are primarily cobalt and molybdenum on alumina, and nickel and molybdenum on alumina. The alumina base is prepared under controlled conditions to give materials of the required surface area and pore volume, and specific pore size distribution. The alumina base is usually in the form of cylindrical extrudates, the size varying from $\frac{1}{32}$ inch to $\frac{1}{8}$ inch in diameter. More recently some manufacturers have supplied extrudate catalyst in shaped form, e.g. American-Cyanamid trilobes, and Akzo-Chemie Ketjen catalysts quadrilobes. These are claimed to give increased superficial surface area for a given nominal extrudate diameter, and also to reduce the

pressure drop obtained. Typical composition and properties of desulphurization catalysts are:

Nickel or cobalt oxides	3–6% wt
Molybdenum oxide	10–20% wt
Surface area	180 250 m^2/g
Pore volume	0.3 -0.5 ml/g
Crushing strength	0.8–2.0 kg/mm
Attrition loss	<2.0% wt

The catalysts are prepared in the oxide form, but the active form is the metal sulphide. During normal operation the catalyst will become sulphided, but to obtain the most active catalysts it is now normal to presulphide the catalyst. This is carried out by adding organic sulphide compounds to the feed at temperatures in the range 200–250 °C, to ensure that most of the metal oxide on the catalyst is converted to metal sulphide before the oxide is reduced to the metal. Commonly used sulphur compounds are carbon disulphide (special facilities must be used with this material), dimethyl sulphide (DMS) and dimethyldisulphide (DMDS). Following presulphiding, operating conditions are then selected to achieve the desired level of desulphurization.

Operating Conditions

The range of operating conditions for hydrodesulphurization is very wide, the choice being determined by the type of feedstock, the desired product sulphur level, availability of hydrogen and its purity, as well as economic considerations.

The following is the normal range of most commercial units:

Reactor pressure	15–175 bars (g)
Reaction temperature	280–420 °C
Space velocity	0.1–12 v/v/h
Gas rate	5–350 m^3/m^3
Make-up hydrogen required	5–170 m^3/m^3

The effect of each of these variables will be discussed in more detail.

Pressure

The choice of operating pressure is dependent mainly on the feedstock and make-up gas purity. In general terms, as the feedstock boiling range increases from naphtha through to residue, the sulphur compounds become more complex and require higher pressures to cause them to react to form hydrogen sulphide and to prevent rapid catalyst de-activation by deposition of carbon.

It can be seen from the reactions involved that hydrogen partial pressure is the important factor, not total reactor pressure, and thus the hydrogen purity of the make-up gas to the process has an effect on the final pressure selected.

Thus, naphtha desulphurizers operate in the range 15–25 bars (g) to give hydrogen partial pressures in the range 6 9 bars, the large difference between the two being due to the degree of vaporization of the naphtha feed. Diesel oil desulphurizers operate at pressures in the range 35–70 bars (g) to give

hydrogen partial pressures of 25 45 bars. Vacuum residue desulphurizers operate in the range 120–175 bars (g), with hydrogen partial pressures from 100–150 bars.

Increases in hydrogen partial pressure will increase the degree of hydrogenation in the normal temperature range. However, the use of temperatures at the high end of the range and choice of lower hydrogen partial pressures will promote naphthene dehydrogenation reactions. The choice of operating pressure must therefore be made with care, to ensure that the process operates under hydrogenation conditions, but the pressure must not be so high that excessive hydrogen is consumed in hydrogenation of the aromatic rings.

Temperature

The effect of an increase in reaction temperature is to increase the rate of reaction and hence increase the level of desulphurization that occurs. Below 280°C reaction rates tend to be slow, and above 410°C undesirable side reactions occur, leading to breakdown of the feedstock to lighter products and excessive deposition of carbon on the catalyst.

As one might expect, the lighter fractions can be readily desulphurized at lower temperatures, but the residues with the more complex compounds require higher temperatures. In the case of naphtha feedstocks higher temperatures can be counter-productive in that temperatures above 340°C can result in the formation of olefins, which may recombine with hydrogen sulphide to form mercaptans. Feedstocks for catalytic reforming require sulphur levels of less than 1 ppm, but on occasions increasing the reactor temperature has increased the sulphur level to 2 ppm, instead of reducing it below the desired level, as might have been expected.

Space velocity

The residual sulphur content from any catalytic desulphurization process is proportional to the space velocity used, i.e. volume of oil processed/volume of catalyst in the reactor. Space velocity controls the reactant residence time, the lighter fractions requiring lower residence times for the reaction to go to completion, compared with the heavier residue fractions. For naphtha feedstocks, space velocities up to 12 v/v/hr could be employed dependent on the temperature and pressure. Normally, however, low space velocities in the range 2–6 v/v/hr are used to minimize temperature requirements. Vacuum residue feedstocks require very low space velocities, and these are normally in the range 0.1–0.5 v/v/hr.

Gas rates

The gas rate chosen is governed by economic considerations. If the supply of hydrogen-containing gas is adequate, a once-through gas flow can be used. This normally occurs with the lighter fractions where the hydrogen consumption is low. For diesel oils and heavier feedstocks it is normal to have a gas compressor to recycle gas back through the reactor. This is necessary to assist in maintaining the desired hydrogen partial pressure in the reactor, thereby ensuring adequate desulphurization and minimizing carbon laydown.

Above a certain gas rate, the change in hydrogen partial pressure will be relatively small. Thus, higher gas rates than are really necessary incur extra heating and cooling costs, which will outweigh the other advantages.

Make-up hydrogen

The quantity of hydrogen required for desulphurization varies widely, dependent on the feed type, feed sulphur content and choice of operating conditions, ranging from about 5 m^3/m^3 for low-sulphur naphtha fractions up to 170 m^3/m^3 for the high-sulphur residue feedstocks. The quantity of gas will depend on the purity of the make-up gas. Hydrogen-containing gas from a catalytic reformer can range from 50 -90% vol hydrogen and from a hydrogen production plant can range from 96–99.99% vol, depending on the purification system used (see previous chapter).

Contaminants, such as carbon oxides and nitrogen, should be kept at a low level. Carbon oxides compete for catalyst surface by conversion into methane and water, and at higher levels may lead to increased carbon deposition. Nitrogen is almost inert under desulphurization conditions and, as its solubility in hydrocarbons is low, it will build up to an appreciable concentration, resulting in a reduction in hydrogen partial pressure. Hydrocarbons present in reformer gas are relatively soluble in the liquid product and, by suitable adjustment of the reactor operating pressure, the desired hydrogen partial pressure can be achieved.

Description of Process

The basic flow diagram of the desulphurization process is shown in Fig. 14. The hydrocarbon feedstock to the process is mixed with recycle gas (or once-through gas in some cases), heat exchanged with reactor effluent, heated to reaction temperature in a furnace and passed to the reactor containing the catalyst. The feed is desulphurized to the desired product sulphur level, heat exchanged with reactor feed, cooled and sent to a high pressure separator. The recycle gas is taken off the top of the separator, make-up gas containing hydrogen added, and the combined gas stream then passes to the suction side of the recycle gas compressor. The recycle gas then mixes with feed and returns to the process. With high pressure units, the separator liquid product may pass to a low pressure separator to remove some of the dissolved gases, before entering the distillation column. This column may vary in complexity, depending on the feedstock to the unit. With lighter feedstocks, a stripper column is used to remove dissolved gases lighter than pentanes, and with heavier feedstocks gasoline and gas oil fractions can be recovered.

The recycle gas from the HP separator is sometimes sent to an amine scrubbing vessel to remove hydrogen sulphide. With high-sulphur feedstocks the level of hydrogen sulphide can build up to high values. This has a detrimental effect by, first, reducing the hydrogen partial pressure and secondly, inhibiting the desulphurization reaction. The choice of including a recycle gas scrubber is normally made from economic considerations.

The desulphurization reaction is exothermic and the heat of reaction is proportional to the hydrogen consumed in the reaction. Under properly chosen

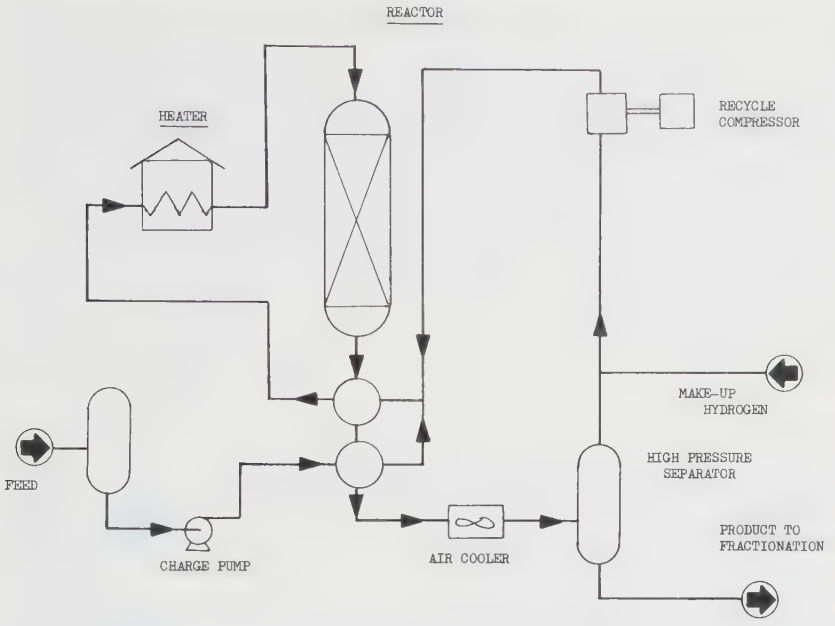


Fig. 14. Catalytic desulphurization process.

operating conditions with saturated feedstocks, where hydrocracking is eliminated, the net heat evolved is relatively small and results in a graded temperature profile through the reactor. However, when unsaturated feedstocks need to be desulphurized, or where very high-sulphur feedstocks (above about 1.5% wt sulphur) are processed, it may be desirable to split the catalyst into one or more beds in the reactor and provide cooling by introducing cold recycle gas into the so-called quench zones between the catalyst beds to compensate for any excessive temperature rise.

The carbon laydown on the catalyst is normally slight, and long on-stream times can be achieved. The carbon can be removed by regeneration, i.e. a simple burn off with air inert gas or air–steam mixtures under controlled conditions. Catalysts subjected to metals deposition cannot be regenerated.

Catalyst Regeneration

Up to the 1970s it was normal to regenerate the catalyst *in situ*. This is carried out by stopping feed supply, depressuring the unit and purging with an inert medium such as nitrogen or steam. The unit is then pressured to between 7 and 20 bars (g) and the reactor temperature raised to about 400°C. Air is introduced at the reactor inlet to give an oxygen concentration of 0.6–1.0% vol and the carbon dioxide produced by combustion of the coke vented from the high pressure separator. Sulphur compounds (SO_2, H_2S) are produced with *in situ* regeneration, and the gases increasingly require treatment to minimize atmospheric pollution.

Since the mid 1970s, it has become increasingly common to regenerate the

catalyst off-site. When de-activated, the catalyst is removed from the reactor under an inert nitrogen atmosphere by specialist contractors. The unregenerated catalyst is dropped from the reactor into containers and sent to a factory specializing in off-site regeneration, and a fresh or freshly regenerated catalyst is charged to the reactor. This procedure has advantages in minimizing unit downtime and eliminating atmospheric pollution.

One firm specializing in off-site regeneration is Catalyst Recovery Inc. A schematic diagram showing the procedure used is given in Fig. 15.

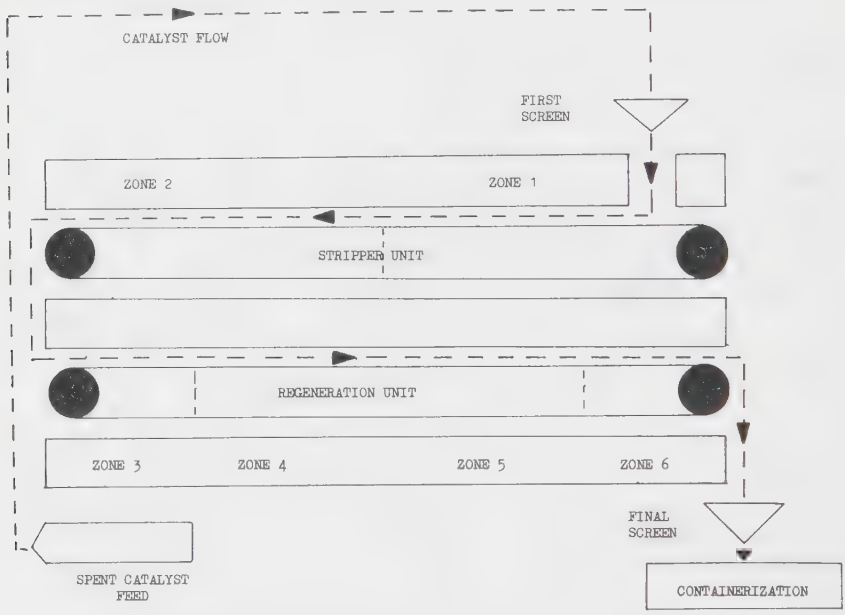


FIG. 15. CRI off-site hydrotreatment catalyst regeneration process.

Spent catalyst is first screened to remove fines and oversize material, including ceramic support balls. The catalyst is then sent to a stripper unit where it is spread out in a thin uniform layer across the width of the belt. This section is required if the catalyst is still saturated with hydrocarbons. These are vaporized under inert conditions before the regeneration process commences. The dried catalyst is then passed to the regeneration zone where the thin layer of catalyst moves through separate and distinct heating zones. This ensures that a smooth temperature gradient is maintained along the length of the belt. The surface temperature of the catalyst can be controlled by varying the bed thickness on the belt, belt speed, and air and fuel input into the burners.

In the first zone, sulphur is burnt off at low temperatures to prevent conversion to highly stable sulphates. Temperatures in the remaining zones are increased to the manufacturer's recommended values to remove the carbon. Finally, the catalyst is cooled, rescreened, and loaded back into containers.

Eurecat is another firm offering off-site regeneration facilities, and the process differs in that a rotating drum is employed instead of a belt.

Typical Process Applications

Naphtha desulphurization

The desulphurization of naphthas prior to catalytic reforming is now mandatory. Desulpurization is virtually complete under relatively mild operating conditions (Table IX), and very long on-stream times, in some cases several years, have been achieved. The catalyst can be readily regenerated, *in situ* or off-site, and regeneration is only required, other than at planned shutdowns, if an upset in process conditions occurs. The catalyst seldom requires replacing other than when contaminated by lead deposition or when more active or more selective new catalysts become available. Lead contamination sometimes occurs after light slop oils have been processed on the naphtha desulphurizer.

TABLE IX
Desulphurization of Naphtha

Process conditions		
Catalyst	Nickel or cobalt/molybdenum-on-alumina	
Temperature	280–350°C	
Pressure	15–30 bars (g)	
Space velocity	2–6 v/v/hr	
Gas rate (once-through or recycle)	40–250 m^3/m^3	
Properties	Feedstock	Product
Specific gravity, 15°C/15°C	0.743	0.740
ASTM distillation, °C		
IBP	85	71
10% vol	107	106.5
50% vol	130	133
90% vol	159	160.5
FBP	172	175
Sulphur content, ppm wt	400	1

In the case of cracked feedstocks, desulphurization is always accompanied by saturation of olefins, resulting in loss of octane number and increased hydrogen consumption.

Middle distillate desulphurization

Desulphurization of middle distillates can reach 80–95 per cent with the correct choice of operating conditions. The change in specific gravity is more marked and the amount of low boiling material produced more significant than with the lighter feedstocks. Process cycle lengths vary with the type of feedstock and the process operating conditions, and range from 3 to 12 months. As with naphtha desulphurization, the catalyst may be regenerated *in situ* or off-site, dependent on the individual refiner's requirements. Typical process conditions and feed and product data are given in Table X.

Feedstocks include straight-run distillates, catalytically cracked cycle oils and visbreaker gas oils. Inclusion of cracked feedstocks requires increased hydrogen make-up and, if the unit was designed for saturated straight-run

TABLE X

Hydrodesulphurization of Middle Distillates (250–400 °C)

Process conditions				
Catalyst	Nickel or cobalt/molybdenum-on-alumina			
Temperature	310–400 °C			
Pressure	30–70 bars (g)			
Space velocity	1–6 v/v/hr			
Gas rate (recycle)	80–450 m^3/m^3			
	Straight-run		Straight-run/cracked	
Typical results	Feed	Product	Feed	Product
Specific gravity, 15 °C/15 °C	0.862	0.851	0.890	0.872
ASTM distillation, °C				
IBP	248	248	206	218
10% vol	275	274	243	241
50% vol	311	308	296	290
90% vol	368	364	365	357
FBP	>370	>370	>370	>375
Total sulphur, % wt	1.25	0.24	2.15	0.26
Total nitrogen, ppm	245	167	260	183
Bromine number	2.6	0.9	5.6	1.3
Aniline point, °C	76.2	78.8	55.4	60.6
Diesel index	55	61	36.0	43.0

distillates, lower liquid space velocities are required to cope with the increased heat release. Saturation of aromatic rings under middle distillate desulphurization conditions is normally not significant.

Residue desulphurization

There are two basic types of residue desulphurization unit, namely fixed bed and expanded or ebullating bed. Fixed bed units are similar to those used for the lighter distillates, i.e. the feedstock and recycle gas containing hydrogen pass downflow through a fixed bed of desulphurization catalyst in the reactor. Expanded bed units, on the other hand, operate with the feedstock passing to the base of the reactor and flowing upwards through the catalyst bed. The reactant flow rate is controlled to cause the bed to expand (see later), and this enables catalyst to be added or withdrawn from the reactor.

Fixed bed units are more suitable for the lower metals content feedstocks, up to 100 ppm, and where lower conversion to lighter products is required. Expanded bed units, on the other hand, are more applicable to the higher metals feedstocks and where more conversion, i.e. hydrocracking, is required. Each process is capable of operation in the range favoured by the other, and the choice between them is based on the individual refiner's economics.

Fixed bed residue hydrotreating

A typical flow scheme for a fixed bed residue hydrotreating unit is given in Fig. 16. The residue feed is filtered, heated, combined with hot recycle gas and charged to a catalytic guard reactor. The guard reactor primarily removes metals from the feed and also does some desulphurization.

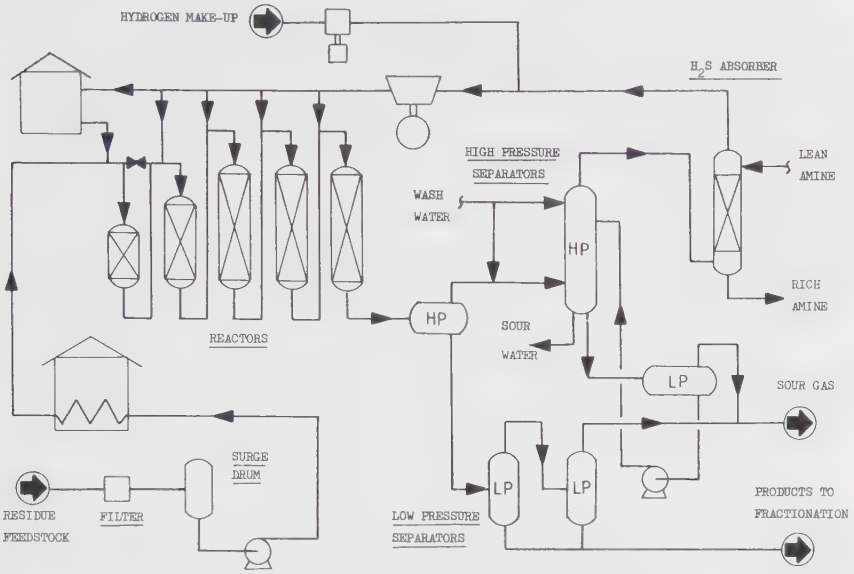


FIG. 16. Union Oil fixed bed residue desulphurization process.

When the pressure drop over this guard reactor reaches a predetermined level the reactor is by-passed. Guard reactor effluent passes to the main desulphurization reactors (typically three or four are used), and cold recycle gas is added between reactors to quench the exothermic heat of reaction. The reactor effluent is then sent to a separator system to separate vapour and liquid at two different temperatures. The vapour from the cold separator has water injected into the stream to remove ammonia to prevent the formation of ammonium sulphide, which can build up to form blockages in the reactor effluent cooler. The vapour from the cold separator is then scrubbed to remove hydrogen sulphide, combined with make-up gas and recycled back to the process. The liquid products from the high pressure separators pass to low pressure separators, also operated at two different temperatures to remove more dissolved gas, and are then sent to product fractionation. Typical product yields are given in Table XI.

The yields shown are for start-of-run. With a fixed bed unit, conversion to lighter products will increase as the run progresses due to the need to increase reactor temperature to offset the decline in catalyst activity caused by metals contamination and carbon deposition.

The run length is typically from 6 to 12 months, and is usually determined by the metals content of the feedstock. The hydrogen consumption will vary depending on the sulphur content of the feedstock.

Process designs are offered by many companies, including Chevron, Exxon, Gulf, Shell, Union Oil, and UOP. The process was originally developed to produce low-sulphur fuel oils, but is being increasingly used to pretreat feedstocks for subsequent processing, such as the delayed coking and residue catalytic cracking processes.

TABLE XI
Typical Yields—Fixed Bed Hydrotreating

Feedstock	Arabian Heavy >343°C residue	Arabian Heavy >538°C residue
Product yields		
C_4 and lighter, % wt	4.7	4.8
C_5–177°C, % vol	1.4	2.0
177 343°C, % vol	11.1	4.4
343 538°C, % vol	57.3	21.6
>538°C, % vol	31.4	74.9
Total C_{5+} Liquid	101.2	102.9
Sulphur removal, %	75–90	75–90
Hydrogen consumption, m^3/m^3	120–140	160–180

Expanded or ebullating bed hydrotreatment

This system was developed originally in the early 1960s to overcome the problems of rapid catalyst de-activation and maintain constant levels of desulphurization. A typical flow sheet of an expanded bed system is shown in Fig. 17.

Feed is preheated in a separate oil heater and mixed with recycle gas rich in hydrogen before entering the base of the first reactor at a temperature 50 60°C below that of the reactor. The oil velocity in the reactor is controlled by recirculating oil through the central pipe and back to the main body of the reactor to maintain the catalyst in an ebullated state. This recirculation results

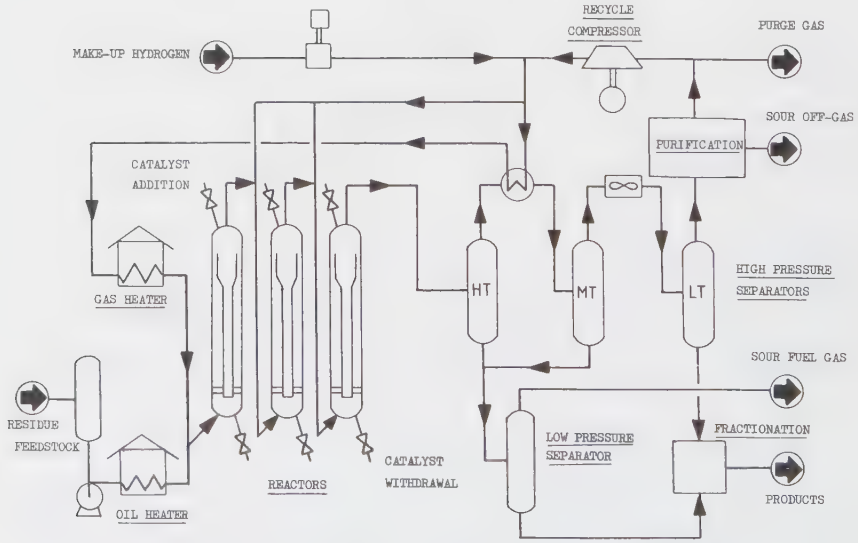


FIG. 17. LC-fining ebullated bed residue desulphurization process.

in a isothermal back-mixed reaction. The heat of desulphurization is used to heat the feed up to the final reaction temperature. As the catalyst is in a fluidized state, it is possible to withdraw spent catalyst and add fresh catalyst on a regular basis. In this way it is possible to maintain the catalyst in the reactor at a constant activity level. As the reactors operate in a back-mixed state, at least two, and sometimes three, reactors are required to achieve high levels of desulphurization. The final reactor effluent passes to a series of separators and coolers to separate the hydrogen-containing gas economically for recycle to the system and the oil products for fractionation. The recycle gas is scrubbed in a high pressure amine absorber to remove hydrogen sulphide, and in addition light hydrocarbons are removed to improve further the purity of the recycle gas.

Expanded bed hydrotreating units are also amenable for the hydrocracking of residue feedstocks as discussed in the previous chapter.

SULPHUR RECOVERY

Many refinery processes, such as catalytic desulphurization, catalytic cracking, and hydrocracking, produce large quantities of sour gas as a by-product. Hydrogen sulphide is commonly removed from this gas and sent to a sulphur recovery unit. This may be done for economic reasons, although nowadays it is usual to remove sulphur to prevent atmospheric pollution. If not removed from the sour off-gases, the hydrogen sulphide would pass into the fuel gas system and be burnt to sulphur dioxide in the refinery furnaces.

The first step in sulphur production is to recover the hydrogen sulphide from the sour off-gases. This is normally carried out at high pressure by a counter-current absorption process using an alkanolamine solution. Amines currently used for this purpose include monoethanolamine (MEA), diethanolamine (DEA), and di-isopropanolamine (DIPA). Hydrogen sulphide is subsequently removed from the amine by heating the solution at low pressure.

A typical H_2S recovery unit is shown in Fig. 18. This comprises an H_2S absorber, often containing a ceramic packing such as Raschig rings, and an amine regenerator. H_2S absorption is commonly carried out at temperatures of 30–40°C and pressures of about 15 bars. Amine regeneration, on the other hand, is carried out at just above atmospheric pressure and at temperatures between 100 and 120°C.

Although several processes have been proposed for sulphur recovery, by far the most common utilizes Claus technology, which involves the combustion of H_2S in a carefully controlled stream of air. Part of the H_2S is oxidized to SO_2 and this subsequently reacts with the remaining H_2S to form elemental sulphur. The basic reactions, therefore, are as follows:

$$2H_2S + 3O_2 \longrightarrow 2SO_2 + 2H_2O$$
$$2SO_2 + 4H_2S \longrightarrow S_6 + 4H_2O$$

The Claus process is carried out at pressures just above atmospheric, and since the reactions are exothermic, waste heat can be recovered by generating useful steam.

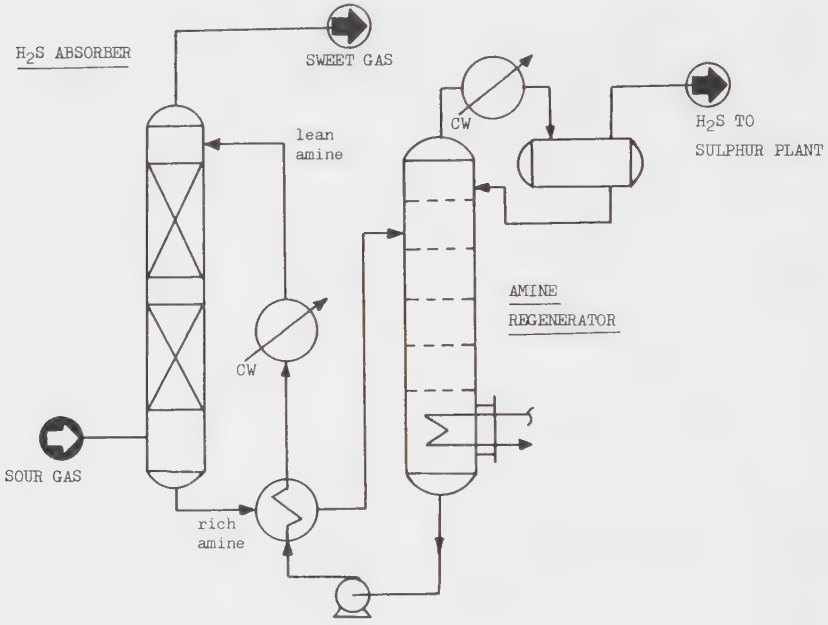


FIG. 18. H_2S recovery unit.

Claus Unit

A typical process flow scheme for a modern Claus unit is shown in Fig. 19. H_2S from the amine regenerator is fed to the furnace together with just sufficient combustion air to satisfy the reaction requirements. Temperatures in excess of 1200°C are reached, and heat is recovered from the reaction gases in the form of high pressure steam generated in the integral waste-heat boiler. Partial conversion of the H_2S to elemental sulphur occurs at this stage. Some of this condenses in the waste-heat boiler and is collected before being sent to the sulphur storage pit.

The reaction gases leaving the waste-heat boiler pass to a condenser where cooling to 150–190°C results in more elemental sulphur being collected. Gases, still containing unconverted H_2S, are then reheated to 200–260°C by means of an in-line burner before passing to a reactor containing a bed of bauxite catalyst, where further conversion takes place. The reaction gases then pass through a second condenser, in-line burner, and reactor, before being sent to the final condenser. Finally, the waste gases are incinerated to oxidize any last traces of H_2S and elemental sulphur before venting to atmosphere via the stack.

The exothermic Claus reaction results in a temperature rise across the first stage reactor of about 30°C and about 15°C across the second stage. Since these temperature rises are an indication of conversion they must be closely monitored. Sulphur recoveries of about 95 per cent can be achieved on modern Claus units depending on the number of condenser/reactor stages employed. To achieve such high recoveries it is always essential to control air rates carefully to maintain the H_2S/SO_2 mol ratio at 2:1.

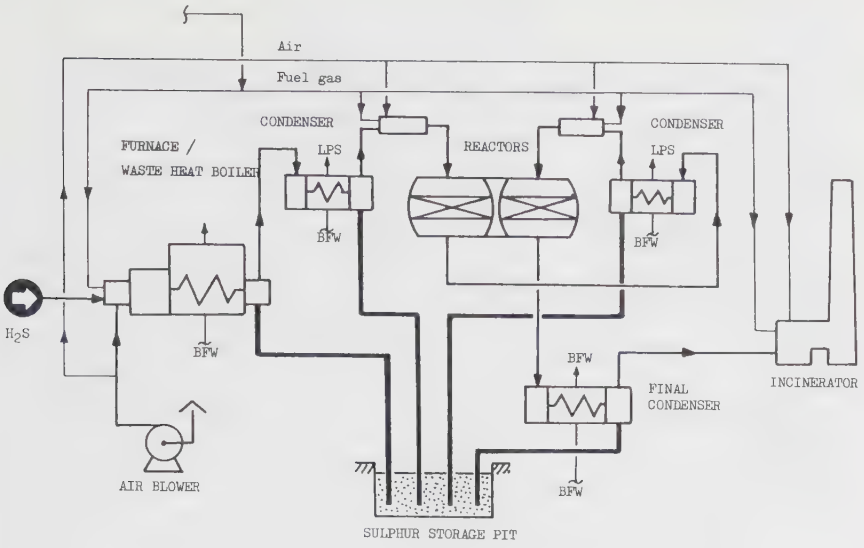


FIG. 19. Sulphur recovery unit.

Claus Tail Gas Units

Modern Claus units achieving 94–96 per cent sulphur recovery closely approach the maximum theoretical yield. The remaining 4–6 per cent unrecovered sulphur is eventually burnt to SO_2 in the incinerator and vented to atmosphere. Where atmospheric emission regulations require even higher sulphur recoveries, a Claus tail gas treatment unit is installed. Many different designs have been developed and it would be beyond the scope of this book to describe them all. However, two of those more commonly used, namely those licensed by Shell and the Institute Français du Petrole, will be described as follows.

SCOT process

The Shell Claus off-gas treatment (SCOT) process shown diagrammatically in Fig. 20 consists of two parts, namely a reduction section and an amine absorption section.

Waste gases leaving the final condenser on the Claus unit are reheated to about 300°C by means of an in-line burner, and after combining with a hydrogen-rich reducing gas, pass to the reactor. Here, the remaining sulphur compounds are reduced to H_2S over a cobalt/molybdenum-on-alumina catalyst. The reactor effluent is then cooled and sent to the H_2S absorber, where H_2S is removed by counter-current scrubbing with an alkanolamine solution. Normally the lean amine supply and rich amine disposal to and from this absorber are connected to the H_2S recovery unit described earlier.

Waste gases leaving the H_2S absorber which now contain only 300 ppm vol H_2S are finally sent to the Claus unit incinerator. It is claimed that the SCOT process increases the overall recovery of sulphur up to 99.8 per cent.

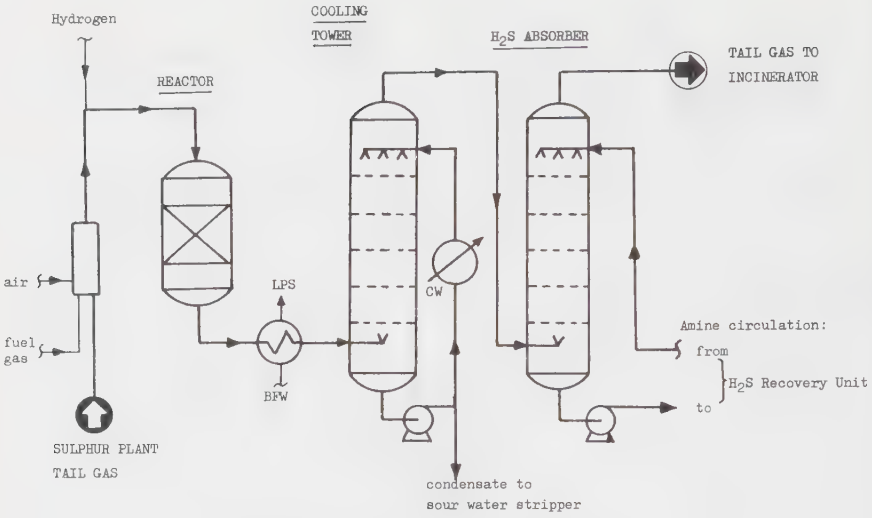


FIG. 20. Shell Claus off-gas treatment process.

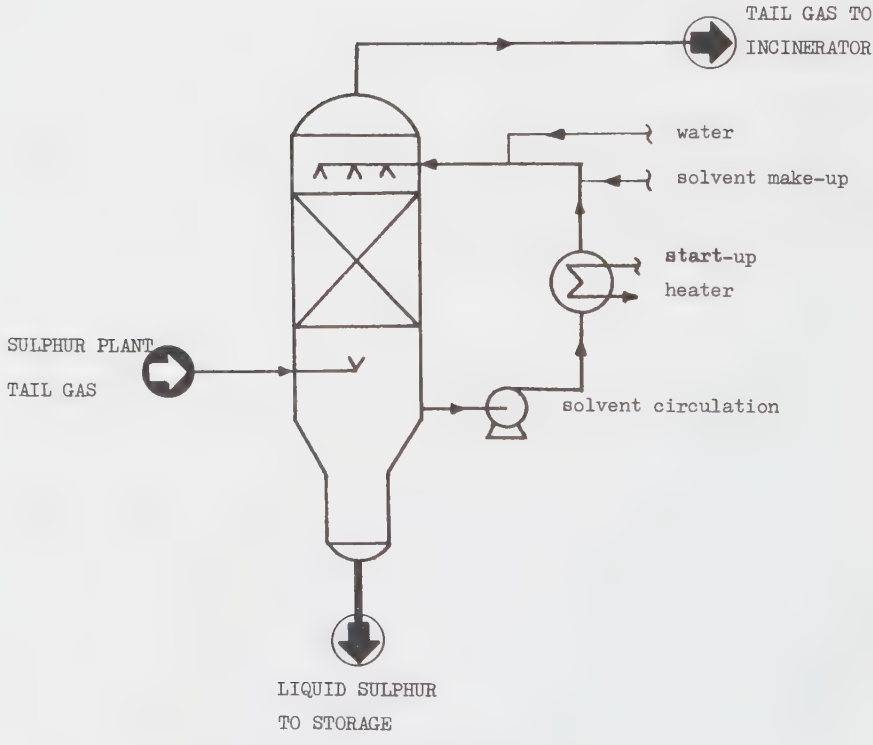


FIG. 21. IFP Claus tail gas treatment process.

IFP process

The IFP process for treating sulphur plant tail gases is a low temperature extension of the Claus reaction. However, in this case the reaction takes place in a catalyst-containing solvent.

The process is shown schematically in Fig. 21. Tail gas from the sulphur plant final condenser enters a vertical packed-tower reactor vessel which is maintained at a temperature of about 125–140°C. Here, the gas contacts a counter-current stream of a proprietary metal salt catalyst dissolved in polyethylene glycol, and the H_2S and SO_2 present in the tail gas react according to the normal Claus reaction. The elemental sulphur so formed is a liquid at reaction conditions, and having a higher density than the solvent, collects in the column base from where it can be continuously withdrawn to the sulphur storage pit.

Since the reaction is exothermic, a small quantity of steam condensate is continuously injected to control reaction temperature. Unlike the SCOT process, the H_2S/SO_2 mol ratio in the sulphur plant tail gas must be carefully controlled at 2:1 in the case of the IFP process to ensure efficient sulphur removal.

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16

Finishing Processes

By S. A. BERRIDGE*

INTRODUCTION

The essential purpose of the primary refining processes described in the three preceding chapters is to produce the required amounts of the various products from the available crudes. The products so obtained are, as a general rule, unsuitable as such for immediate use, for a variety of reasons, such as inadequate performance, instability in storage, objectionable odour or appearance, and contamination with water or particulate matter.

Secondary refining processes, referred to as finishing or treating processes, are therefore required to make products acceptable with respect to the above criteria. A list of undesired constituents and their sources is given in Table I, while Table II lists the objectives and principles involved in treating the various refinery intermediate and final products.

It is almost universal practice to group the main finishing concepts as shown in Table III, and to treat the products by one or other of the general classes of processes given in Table IV. This chapter will therefore be based on this general framework, and processes will be discussed in terms of need, history, present practice, and operating characteristics.

A further important new factor is the increasing need to refine residual fuel oil. This results from two important demands; first the environmental protection pressures to restrict emissions of acid gases, and secondly the market demand to upgrade residual fuels to more acceptable products.

I REFINING OF DISTILLATE FUELS

In describing the processes under the headings listed in Table III there is unavoidably a certain amount of overlapping, and processes or substances will appear under more than one heading. For example, hydrogen sulphide and mercaptans belong under both 'removal of objectionable gases' and 'removal of objectionable odours'. Those finishing processes, which are concerned primarily with performance improvement, are discussed later in a separate section.

Removal of Objectionable Gases

Table V lists processes used for the removal of objectionable gases. They are designed primarily to remove hydrogen sulphide, but most of them also remove other acid gases. Caustic washing in addition also removes acidic liquid constituents such as phenols and fatty and naphthenic acids, but these substances primarily affect performance and storage stability.

* See Acknowledgement.

TABLE I
Undesired Constituents and Their Sources

Mercaptans	Present in most crudes, and may be formed during processes for the decomposition of organic sulphur compounds.
Hydrogen sulphide	Some present in sour crudes, but mostly formed by thermal and catalytic decomposition of sulphur compounds during distillation, cracking, reforming, etc.
Elemental sulphur	Very rarely present. Usually formed from hydrogen sulphide by oxidation owing to the absorption of air during intermediate storage.
Carbonyl sulphide	Probably all formed during processing, particularly by thermal and catalytic cracking.
Neutral sulphur compounds	Sulphur compounds originally present in the crude undergo numerous changes in the course of processing, which alter their type, molecular weight, distribution, etc. Known to occur are carbon disulphide, sulphides, disulphides, thiophens.
Water	Primarily originates from free water in crude. Also introduced from external sources during processing and storage.
Nitrogen bases	Probably result from thermal or catalytic decomposition of more complex nitrogen compounds in the crude.
Compounds causing discoloration	These probably include numerous materials such as sulphur compounds, nitrogen bases, phenolic materials, and hydrocarbons (fulvene series) largely formed in the course of processing. Caused by oxidation and polymerization.
Gum and gum-forming constituents	The gum-forming constituents appear to consist primarily of the cyclic and conjugated diolefins and secondly of other highly reactive unsaturates. These are formed almost entirely as a result of thermal or catalytic cracking or reforming. Other materials, such as some sulphur compounds, acidic materials, and metallic contaminants, all formed during processing act as promoters of gum formation.
Organic peroxides	Are formed by oxidation of hydrocarbons, with the olefins and diolefins being particularly sensitive. Peroxides are deleterious in that they adversely affect gum stability and antiknock performance, promote lacquering, etc.
Naphthenic and phenolic acids	Some have been found in crudes, and others are believed to be formed in processing (especially during cracking) by decomposition of more complex oxygen compounds in the crude.
Fatty acids	Thermal cracking is particularly known to lead to formation of formic acid, acetic acid, etc.
Carbon dioxide	Formed during cracking, particularly catalytic cracking. Present also in natural gas.
Ammonia and hydrocyanic acid	Formed during catalytic cracking and hydrogen treating operations.
Aromatics	Those occurring in straight-run products exist as such in the crude. Those in cracked or synthetic products may either have been formed in processing or have been present in the crude.
Asphaltenes and resins	It is unlikely that straight-run residue contains only unchanged components originally present in the crude. Some of the asphaltenes and resins found in straight-run residues are probably formed by incipient cracking during distillation of the crude. The asphaltic matter present in cracked residues is largely formed during the cracking operation.
Wax	Straight-run waxes are present as such in the crude, whereas those occurring in cracked or synthesized products may have been formed in processing.

Caustic Washing

Washing with caustic soda or potash is used to remove a variety of substances, as listed in Table VI. The process is extremely simple, as can be seen from Figs 1(*a*) and 1(*b*). For gases the equipment consists essentially of a wash tower through which the gases are bubbled, filled to the required level with aqueous caustic soda or potash. For liquids the caustic and the stock to be treated are mixed in a horizontal drum and give product and spent caustic layers. A two-stage system may be used. An identical system may also be used to water wash the product to remove final traces of alkali.

Removal of hydrogen sulphide

Hydrogen sulphide has to be removed from products because it is toxic, foul smelling, and corrosive. Moreover, it may seriously contaminate regenerative treating solvents such as a solutizer used for final sweetening of the product.

Scrubbing with caustic soda is still the most widely used process for the removal of hydrogen sulphide, mainly because it simultaneously removes other constituents, as listed in Table VI, which are either undesirable or are recovered for other use or for sale. However, there is no known cheap method of regenerating the spent soda, and if hydrogen sulphide is present in gross

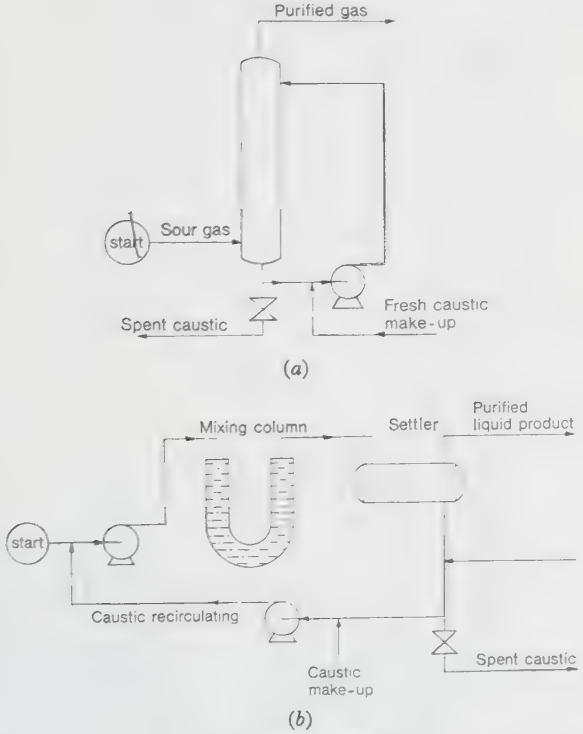


FIG. 1 (*a*) H_2S removal from gases by caustic washing, (*b*) H_2S removal from liquids by caustic washing.

TABLE II

Specific Objectives and Principles of Treating Various Refinery Intermediate and Final Products

Objective of treatment	Product treated										Treatment by partially or totally segregating, removing, or converting													
	Gas	Propane/propylene	Butane/butylene	Gasoline	Special naphthas	Kerosine	Gas oil	Lubricating oil	Residue	Hydrogen sulphide	Mercaptans	Carbonyl sulphide	Total sulphur	Water	Nitrogen bases	Colour and potential colour	Gum and potential gum	Aromatics	Asphaltenes, resins	Wax	Phenolic compounds	Naphthenic acids	Hydrocarbons
(A) To minimize:																								
Acidity		×	×	×	×	×	×	×	×	×	×		×									×	
Carbon residue							×	×											×				
Catalyst deactivation:																							
Alkylation			×							×	×		×	×	×								
Clay treatment				×											×								
Hydrogenation			×							×	×		×										
Isomerization			×	×							×			×									
Polymerization		×	×							×	×			×	×								

Corrosivity		×	×	×	×	×	×	×		×	×		×									×
Gum formation				×											×		×				×	
Interaction with paints					×					×	×		×									
Noxious combustion products	×	×	×	×		×	×			×	×		×									
Plugging of LPG regulator valves		×	×									×		×								
Toxic vapours	×	×	×	×	×	×	×			×	×	×										
(B) To improve:																						
Burning characteristics						×	×						×					×				×
Colour and colour stability				×	×	×	×	×							×	×			×*		×	
Lead (TEL) susceptibility				×	×					×	×		×									
Lubricating oil properties								×										×	×	×		
Octane rating				×						×	×		×									
Odour		×	×	×	×	×	×	×		×	×		×		×			×				×
Pour point							×	×	×											×		
(C) To segregate for sales or further processing:																						
Alkyl phenols				×			×															
Hydrogen sulphide	×	×	×																			
Mercaptans			×	×																		
Naphthenic acids						×	×															
Nitrogen bases				×																		
Sulphonates							×	×														

* Lubricating oil only.

TABLE III
Main Finishing Concepts

Removal of objectionable gases
Removal of objectionable odours
Improvement in storage stability
Improvement in performance characteristics
Removal of water and particulate matter
Segregation of wax
Segregation of aromatics
Improvement of colour

TABLE IV
Classification of Finishing Processes

Solvent extraction
Chemical oxidation
Acid treatment (now largely obsolete)
Hydrogen treatment
Clay refining (now largely obsolete)
Molecular sieves
Dehydration and filtration

amounts, as it frequently is in crude gases, especially the C_2–C_3 fraction, a regenerative method of extraction such as the Girbotol process is more generally used. Such a process is economically more attractive than caustic washing, but the latter may still be required as a final cleaning-up operation to remove the last traces of hydrogen sulphide. This is particularly desirable when the treated gas is being sold to a chemical works or a public gas company. The combination of the two processes not only provides a very low H_2S content economically, but also safeguards against high sulphur contents in the treated products should there be a temporary failure of the regenerative treating plant.

TABLE V
Processes for the Removal of Objectionable Constituents

Caustic washing
Girbotol
Shell ADIP
Hydrofining
Glycol-amine–Malaprop
Hot carbonate
Giammarco-Vetrocoke
Shell Sulfinol
UOP Merox
Howe-Baker mercapfining
Merifining

TABLE VI
Constituents Removed by Caustic Washing

Hydrogen sulphide
Carbon dioxide
Carbonyl sulphide
Lower aliphatic mercaptans
Phenols and aryl mercaptans
Fatty acids
Naphthenic acids

In the caustic washing of gases rather weak solutions of 2–10 per cent weight sodium hydroxide have to be used to prevent the deposition of sodium hydroxide crystals. The reaction proceeds almost to the complete conversion of NaOH into NaHS.

Traces of hydrogen sulphide often appear in fractions much heavier than the C_2–C_3 fraction, because of a slight breakdown of sulphur compounds owing to pyrolysis during redistillation or a similar operation. Caustic soda may be employed for its removal.

Mistrot and Kilgour have reported[1] that a solid bed of potassium hydroxide is successful for removing low concentrations of hydrogen sulphide from liquid propane that does not need drying.*

* Separate lists of References and a Bibliography have been placed at the end of each of the three main sections of the chapter. Each group of References is numbered separately.

Removal of carbon dioxide

Carbon dioxide is frequently found in natural gas, and is also present in the products from catalytic crackers, since regenerated catalyst always carries with it a small quantity of carbon dioxide. Its removal is rarely a direct aim but the major part of it will be removed by a caustic wash applied for the removal of hydrogen sulphide. When CO_2 removal is a direct aim one of the regeneration processes listed in Table V would normally be used.

Removal of carbonyl sulphide

Carbonyl sulphide is produced by both thermal and catalytic cracking. Its boiling point is $-50°C$, and thus it occurs chiefly in the propane/propylene fraction, and also to some extent in the ethane/ethylene fraction. It has to be removed from propane/propylene intended for feed to a polymerization plant or for sale as LPG, since it is liable to hydrolyse to hydrogen sulphide and carbon dioxide, and will form gums by reaction with olefins.

The conventional method of removing it is by washing with dilute caustic soda. The reaction proceeds in two stages: a slow mass transfer of carbonyl sulphide from the hydrocarbon to the aqueous phase, favoured by low caustic strength, followed by hydrolysis to carbon dioxide and hydrogen sulphide, favoured by high caustic strength. Since the first reaction is the rate-limiting one, a low concentration of about 3 per cent weight is found to be the best.

Removal of lower aliphatic mercaptans

Mercaptans combine with caustic alkalis to form mercaptides according to the equations $RSH + NaOH = RSNa + H_2O$. The reaction is reversible, and with increasing molecular weight of the mercaptans there is a sharp fall in the conversion into mercaptide, as shown in Table VII.[2]

It is therefore commercially feasible to use plain caustic soda solutions for the removal of only methyl, ethyl and to some extent, propyl mercaptans, and thus only C_3, C_4, C_5, amd occasionally C_6 fractions may be desulphurized in this manner.

Contacting hydrocarbon and caustic may be carried out in multi-stage mixer/settler equipment, for which two stages normally suffice; alternatively a packed tower may be used. As the mercaptan concentration builds up in the

TABLE VII
Extraction of Mercaptans with Caustic Soda

Mercaptan	Boiling point (°C)	Relative distribution coefficient
Methyl	7	213
Ethyl	37	80
n-propyl	67	10.7
n-butyl	97	3.0
n-amyl	126	1.0

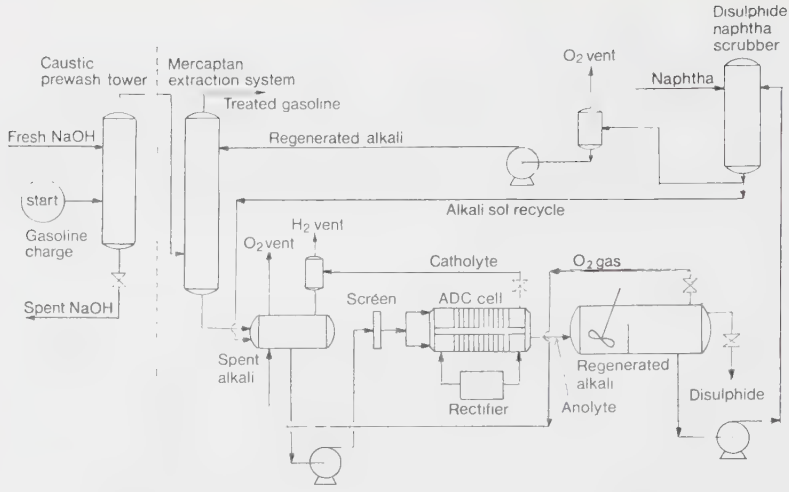


Fig. 2. American Development Corporation's electrolytic oxidation process.

caustic the efficiency of extraction falls off, and since this normally sets a limit to efficient extraction, it is frequently economic to regenerate the spent caustic when only 15–30 per cent has been converted into mercaptides. This may be accomplished easily by steam stripping in a bubble-cap column. The mercaptans from the top of the column may be disposed of by burning in an adjacent furnace, or recovered as 'stenching' material for bottled gas or as a raw material for chemical manufacture.

Alternatively, regeneration of the spent acid may be accomplished by air blowing, with or without the use of an oxidation catalyst. Disulphides are formed which may be separated by gravity or by naphtha washing, and then disposed of by whatever method is most suitable. This method of regeneration excels because of the relative absence of corrosivity.

It is also possible to regenerate the spent caustic by an electrolytic oxidation process (Fig. 2) developed by the American Development Corporation.[3] The alkali solution is recycled through the regeneration equipment in order to limit the degree of regeneration per pass, otherwise unacceptable polarization of the electrodes will occur.

Girbotol Process

Hydrogen sulphide and carbon dioxide readily combine with aqueous solutions of certain alkanol amines at temperatures usually close to ambient, and may be driven off from the fat solutions by heating to about 100°C. The reaction with hydrogen sulphide is essentially:

$$2RNH_2 + H_2S = (RNH_3)_2S$$

The reaction forms the basis of the Girbotol process, discovered by Bottoms in 1930.[4] The amines normally used are the mono-, di-, and tri-ethanolamines and methyl-di-ethanolamine.

Mono-ethanolamine has a higher absorptive power than has di-ethanol-amine for hydrogen sulphide and carbon dioxide per volume of treating

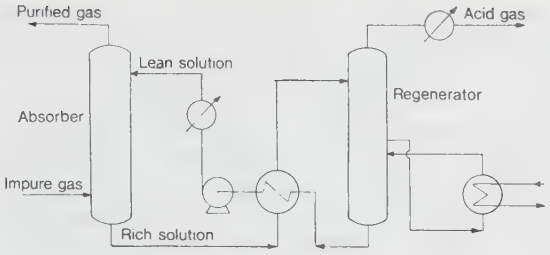


FIG. 3. Girbotol process.

solution, but has the disadvantage that any carbonyl sulphide in the gas combines irreversibly with it, which is not the case with di-ethanolamine. The tri-ethanolamines have poorer absorptive power but are more selective, removing carbon dioxide only to a relatively small extent. The treating solution contains from 15 to 30 per cent weight of amine.

The general arrangement of the plant is shown on Fig. 3; conventional equipment is used, comprising a bubble-cap tower, if gases are to be treated, or a packed tower for liquids, together with a bubble-cap tower for regeneration. Treatment is at line pressure, but care must be taken to see that the treating temperature is 5 to 10°C above the dew-point of the gas to ensure that no hydrocarbon liquid condenses out in the plant. In certain cases it may be worthwhile to arrange the plant for split flow of the treating liquor.

The Girbotol process is perhaps the most widely used method for the regenerative removal of hydrogen sulphide from both gases and liquids. Its use is not confined to refineries; its simplicity and trouble-free nature combine to render it an excellent process for oilfield treatment of natural gas and LPG.

Utility requirements are low and the plants are flexible in operation, readily yielding products containing only very small amounts of hydrogen sulphide. Where the hydrogen sulphide content must be reduced to only one or two parts per million or lower, it is usually more economic to follow the Girbotol process with a non-regenerative soda wash rather than to incur the very high solvent circulation and very complete regeneration needed if the Girbotol process alone has to meet requirements.

In common with other treating processes, the Girbotol process is liable to a number of operating troubles.[5] Foaming of the amine solution may result in serious reduction of capacity and loss of solution. This may be caused by certain organic acids in the feed which combine with the amines to form soap-like compounds. Foaming may be much reduced either by prior treatment of the feed to remove most of the offending acids, as for example by water washing, or by the addition of anti-foaming agents, such as oleyl alcohol, to the solution. The use of a prior water wash will not be without attendant problems if much hydrogen sulphide is present, since equipment will be needed for the disposal of the sour water arising from the operation.

Sometimes sludge may build up in the solution to the extent of blocking columns, heat exchangers and lines. The sludge may originate from fine dust in the feed gas, and if the flow of gas is high, as it frequently is, even small concentrations of dust will rapidly cause trouble. Iron sulphide produced by sulphur corrosion of equipment upstream of the process is an example of such a

dust, and troublesome quantities of iron sulphide and sulphur dust in natural gas have been reported. A preliminary water wash may be used to prevent dust entering the plant, or the solution may be kept relatively free of sludge by filtering or centrifuging a slipstream.

Special precautions must be taken when the feed gas contains oxygen, as when treating gases from a catalytic cracker. Amine thiosulphates are then formed and since they are relatively heat-stable, the absorbing capacity of the solution will be correspondingly reduced. The cure is to add sodium hydroxide or carbonate to the solution whereby the amine is liberated and the thiosulphate fixed as sodium thiosulphate. If only traces of oxygen are present in the feed no further action may be necessary, since the natural rate of loss of amine solution may be sufficient to prevent the build-up of a high concentration of thiosulphate solution by either steam distillation or solvent extraction.

Traces of organic acids occasionally present in refinery gases may also accumulate in the solution and combine with the amine, thus reducing its absorptive power. As with oxygen, the remedy is the injection of caustic or carbonate.

The choice of the proper amine and solution strength depends on the composition of the gas to be treated, the percentage of hydrogen sulphide and/or carbon dioxide in the gas, and the final purity desired. In many cases it is possible to attain a moderate degree of selectivity by the proper choice of solutions and operating conditions where complete hydrogen sulphide removal is desired and carbon dioxide removal is not required. Girbotol plants are customarily designed to purify gases at their full line pressure, and the pressure drop through the equipment will not normally exceed 5 to 10 psi.[6]

Shell ADIP Process

The Shell ADIP process is a regenerative process for the absorption or extraction of H_2S, CO_2, and COS from gases and from LPG. The solvent is usually an aqueous solution of di-isopropanolamine (DIPA). Methyl-di-ethanolamine (MDEA) may be preferred because of its higher selectivity, which results in a better composition of the feed to the sulphur recovery unit.

The main areas for application of the process are shown below:

Streams to be treated	Contaminants removed
Refinery gases Fuel gas, HDS recycle gas, catalytic cracker dry gas	H_2S
Natural gas liquids, liquefied petroleum gas	H_2S, COS
Reduced Claus off-gas (SCOT process)	H_2S, COS (partly)
Gas from oil or coal gasification in combined-cycle power stations	H_2S, CO_2 (partly)
Natural gas	H_2S, CO_2 (high CO_2/H_2S ratio)

The advantages of the Shell ADIP process accrue from the specific properties of the ADIP solvent (DIPA and MDEA).

DIPA. The basicity of di-isopropanolamine is such that it gives a more favourable balance between absorption capacity and energy requirement for its regeneration than other alkanolamines. Consequently, in practically all applications the steam consumption of the ADIP process for a certain treating performance is lower than that of processes using other solvents. Furthermore, the corrosivity of the ADIP solution is low, so that carbon steel can be used as a material for construction of the units.

The capabilities of effectively and reliably removing H_2S from refinery gas streams at relatively low steam consumption, with equipment that can be constructed from carbon steel, makes the Shell ADIP process a highly efficient process for such applications.

The ADIP solution can also be used for the removal of carbonyl sulphide (COS) from LPG or natural gas liquids. For this purpose a mixer-settler system is used as a contacting device for the liquid hydrocarbon stream and the solvent. Regeneration is carried out in a normal ADIP regenerator. A COS removal step can therefore easily be integrated with the gas- and liquid-treating ADIP units at the same location, using a common regenerator.

The ADIP solution can also be utilized to achieve an appreciable selectivity in the absorption of H_2S with respect to that of CO_2. The rate at which ADIP solution absorbs H_2S is approximately equal to that of other solvents that are normally used. The rate at which CO_2 is absorbed, however, is substantially lower than that in other alkanolamine solutions. This difference in absorption kinetics makes it possible to design the ADIP process in such a way as to provide an appreciably higher selectivity between H_2S and CO_2 removal than is possible with other solvents.

The selectivity is of specific advantage for those applications in which H_2S has to be removed from gases containing CO_2 and the removal of CO_2 is not desired. An example of such an application is the absorption step in the Shell Claus Off-gas Treating (SCOT) process.

Another example in which the selectivity for H_2S removal with respect to CO_2 removal is an advantage is purification of gas obtained by the partial oxidation of fossil fuels that are used for the generation of electricity in combined-cycle power stations. Since the CO_2 is only partly removed from the gas, the solvent circulation of the treating unit can be smaller, and the acid gas which is recovered from the regenerator is richer in H_2S. This facilitates its conversion into elemental sulphur.

MDEA. Recently, another amine has been adopted for the ADIP process, namely methyl-di-ethanolamine (MDEA). This tertiary amine is even more selective than DIPA owing to the fact that bicarbonates are formed when reacting with CO_2. This reaction is much slower than the reaction of CO_2 with a secondary amine (like DIPA) forming carbamate.

At present the use of MDEA can result in considerable savings, especially in cases with a low H_2S and a high CO_2 content in the feed gas, e.g. in SCOT units in which the tail gas from the sulphur recovery unit has a high CO_2 content.

The ADIP process was first applied in 1959. At present there are well over

170 units in operation or under construction, excluding those incorporated in the Shell Claus Off-gas Treating process. Eight units are equipped for the removal of carbonyl sulphide from LPG. The total capacity is approximately 60 million Nm^3/sd and 29 000 t/sd for gas and liquid treating, respectively.

Glycol-amine Process

Frequently a gas must be dried as well as purified of hydrogen sulphide, as with natural gas for domestic use where water must be removed to prevent condensation in the line and the formation of solid hydrates at low temperatures. The two operations are combined in the glycol-amine process which uses a mixture of di- or tri-ethylene glycol, mono- or di-ethanolamine, and water as the solvent. The amines and glycols are good drying agents, but the amines are considerably more viscous than the glycols, hence the mixture. Selectivity for the removal of hydrogen sulphide in the presence of carbon dioxide is achieved by the use of methyl-di-ethanolamine.

It is claimed that even when removal of water is not required the process can still show advantages over others on respect of the production of very pure gas, low initial investment, low steam consumption, and less tendency to foam. Disadvantages are corrosivity developed on regeneration and the rather large amount of hydrocarbons dissolved by the solution.[5]

Malaprop Process[7]

Process advantages claimed for the Malaprop process which uses diglycol-amine (DGA), include: (a) single-step removal of COS from very high levels (4000 ppm) to below 2 ppm, (b) low energy and chemical consumption, (c) utilization of simple equipment, and (d) operation typical of other amine systems.

A process disadvantage is that it requires dehydration of the propane; however, this is not significant.

A number of reactions occur to varying degrees in this process. The first reaction is hydrolysis of carbonyl sulphide to yield hydrogen sulphide and carbon dioxide, with the subsequent removal of acid gas components by conventional sweetening methods.

$$COS + H_2O \longrightarrow CO_2 + H_2S$$

An intermediate reaction involves the direct combination of COS with DGA to form a urea degradation product of DGA and H_2S. The hydrogen sulphide is removed by DGA through conventional acid gas absorption.

The third reaction is the reclaiming reaction in which the urea complex and water react to form DGA and CO_2. Obviously, the 'degradation' reaction and the reclaiming reaction must be balanced to maintain solution quality.

Propane treating in the Malaprop process (Fig. 4) is accomplished by contacting propane and DGA in a counter-current fashion in a liquid/liquid contactor. The amine phase is the continuous phase, with the interface held at the top of the tower. Sweetened propane flows through a water wash to lower amine loss, and finally to alumina dryers for dehydration. Propane vapour,

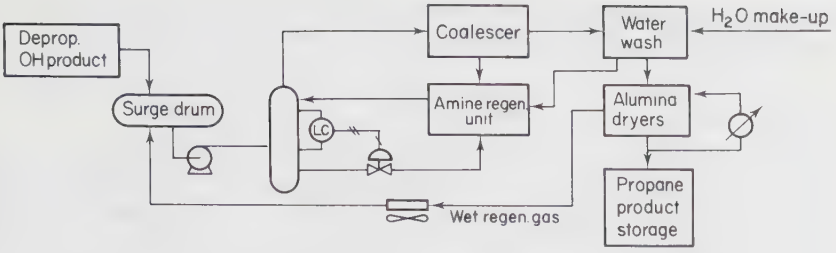


FIG. 4. Malaprop process—propane treating.

used as regeneration gas for the dryers, is recycled to the front end of the process.

Amine regeneration (Fig. 5) is similar to most amine regeneration units,[9] using a flash tank for the removal of entrained propane and a carbon filter for solution maintenance, but certain design modifications have been incorporated to accommodate specific requirements.

Hot Carbonate Process[9]

The hot carbonate process, in which either sodium or potassium carbonate is used, is essentially for the removal of carbon dioxide, but fair extraction of hydrogen sulphide is also achieved. The equipment consists of a conventional absorber and steam-heated regenerator, but no solvent/solvent heat exchangers are required, since both absorption and regeneration operate at virtually the same temperature. The process is ideally suitable for the removal of carbon dioxide from natural gas where only moderate removal, say down to 1 per cent volume, is frequently all that is required. The process may still be attractive for more complete removal of carbon dioxide or hydrogen sulphide if it is followed by a Girbotol or similar process.

The advantages of the process are low plant construction costs, low steam

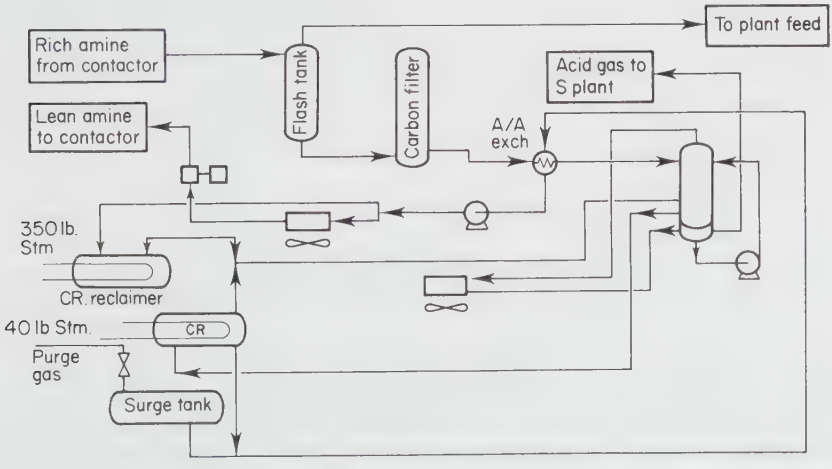


FIG. 5. Malaprop Process –amine regeneration.

consumption, negligible chemical consumption, and insensitivity to oxygen in the feed, which in an amine plant may cause severe corrosion.

Giammarco-Vetrocoke Process[10]

A disadvantage of the conventional hot carbonate process is the slow rate of absorption and desorption of carbon dioxide. Giammarco discovered that the rates could be considerably increased by adding to the carbonate solution appreciable amounts of the trivalent acids of arsenic, selenium, or tellurium, and thus developed the Giammarco-Vetrocoke process in which arsenic trioxide is normally used.

Compared with the conventional hot carbonate process, both absorption and regeneration are less, and far less steam is used for regeneration. Regeneration may be effected under pressure, and air may be used instead of steam for stripping. Arsenic trioxide is an excellent corrosion inhibitor, and hence the whole plant may be constructed of mild steel.

Giammarco also discovered that a solution of alkali arsenites and arsenates possessed great flexibility for the absorption of hydrogen sulphide. By adjusting the composition and acidity of the solution, either selective absorption of hydrogen sulphide in the presence of carbon dioxide could be obtained or both could be absorbed simultaneously.

Shell Sulfinol Process

The Shell Sulfinol process is a regenerative process for the absorption of H_2S, CO_2, COS, and mercaptan from gases. It has been developed specifically for treating large quantities of gas available at elevated pressures.

The Shell Sulfinol process is unique in this class of processes because it uses a mixture of solvents, which allows it to behave as both a chemical and a physical absorption process. The solvent is composed of Sulfolane, di-isopropanol amine, and water.

The acid gas loading of the Sulfinol solvent is higher and the energy required for its regeneration lower than those of purely chemical solvents. At the same time it has the advantage over purely physical solvents that severe purity specifications can be met more easily.

The Shell Sulfinol process is characterized by the following features:

(a) Reduction of H_2S plus organic sulphur to natural gas pipeline specification;
(b) Low steam consumption and solvent circulation;
(c) Low corrosion rates;
(d) Good absorption of organic sulphur components;
(e) Smaller equipment due to non-foaming tendency;
(f) High on-stream factor;
(g) Selective removal of H_2S in some natural gas applications.

The process may be briefly described as follows (Fig. 6):

The feed gas is contacted counter-currently in an absorption column with the Sulfinol solvent. The regenerated solvent is introduced at the top of the absorption column at reduced temperature and leaves this column at the

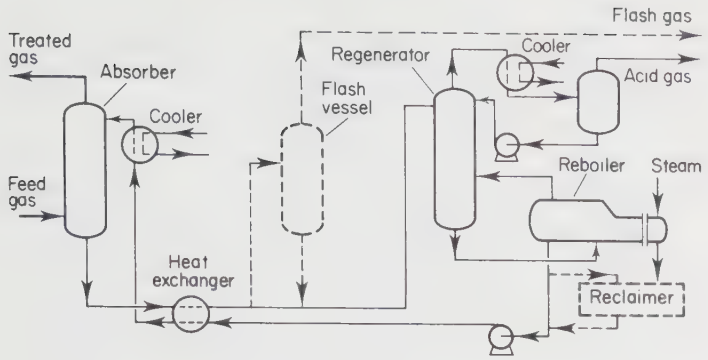


FIG. 6. Shell Sulfinol process.

bottom. The rich solvent is heated by heat exchange with the regenerated solvent from the bottom of the regenerator and is fed to the regenerator, where it is further heated and freed of the acid gases with steam. After flowing through the heat exchanger, the regenerated solvent is cooled by heat exchanger with water or air and then introduced into the absorption column. Subsequently, the acid gases removed from the solvent in the regenerator are cooled with air or water, so that the major part of the water vapour that they contain is condensed. The sour condensate is reintroduced into the system as a reflux. In this way the acid gas is made available for further processing.

The use of a flash vessel is optional; it depends on the heavier hydrocarbons content of the feed gas and further requirements with respect to processing of the acid gas. Also optional is the use of a reclaimer; this depends on the amount of non-regenerative compounds in the solvent.

The economic advantage of the Shell Sulfinol process is the largely reduced solvent circulation and regeneration steam consumption.

As stated, the Sulfinol solvent is a mixture of di-isopropanol amine (DIPA), Sulfolane (tetrahydrothiophene 1-1 dioxide), and water, which can be used in different concentrations, depending on the specific application.

Solvent	Streams to be treated	Contaminants removal
I	Natural gases Oil and coal gasification	H_2S, CO_2, COS, RSH, and organic S compounds
II	Natural gases	H_2S, CO_2 (partly)
III	LNG feedstock, hydrogen manufacture, synthesis gas	CO_2

In formulation II H_2S is selectively removed.

The absorption equilibria that distinguish the sulfinol from aqueous amine and other solvents are of interest in understanding the process. Figure 7 is a plot of the H_2S equilibrium partial pressure against solvent loading for several solvents. Water is obviously a poor solvent; even at high partial pressures it dissolves only a little gas. Aqueous mono-ethanolamine (MEA) shows good

TABLE VIII

Typical Operating Data for Shell Sulfinol Units

Feedstock		Crude synthesis gas from partial oxidation of heavy fuel	Crude synthesis gas after CO shift conversion	Oxo synthesis gas	Natural gas
Feed gas flow	Nm^3/h	14 100	19 000	15 300	52 500
H_2S content	% vol	0.46	—	0.36	18.89
CO_2 content	% vol	4.90	31.40	5.20	2.14
COS content	ppm (vol)	216	–	125	
Mercaptane		—	—		375 mg/Nm^3
CS_2		—	—	—	
Absorption pressure	kg/cm^2 abs.	29	23.5	39.5	59.0
Absorption temperature	°C	22	20	41	43
Number of trays in absorption column		35	30	40	27
Treated gas:					
CO_2	ppm (vol)	<500	125	25	<2% (vol)
H_2S	ppm (vol)	3	—	0.5	7
COS	ppm (vol)	15	—	0.3	—
L.P. steam consumption	mt/mt acid gas removed	1.64	1.15	1.90	1.80
Electricity consumption	kWh/mt acid gas removed	21	13	30	20

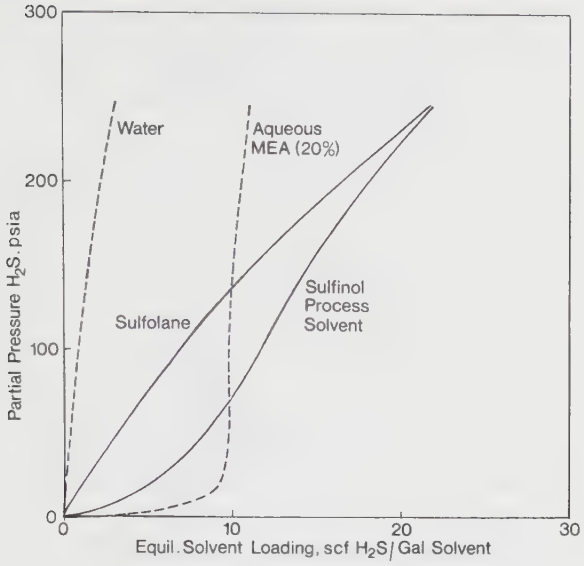


FIG. 7. H_2S absorption isotherms.

solvency at low partial pressures because of the acid/base reaction of amine with hydrogen sulphide, but after the alkalinity has been consumed further increase in partial pressure results in no more increase in solubility than is shown by water. Thus aqueous MEA is a good solvent for applications involving low partial pressures of acid gas, but is less attractive for handling high concentrations. In practice aqueous MEA is seldom loaded beyond 4.5 cu ft/gal because of operational problems associated with corrosion and foaming. Sulfolane is a very good solvent for acid gases, its capacity for hydrogen sulphide being nearly eight times that of water at all partial pressures. It is also a good solvent for mercaptans and carbonyl sulphide.

When an alkanolamine is added to sulfolane, the alkalinity of the amine leads to high solubility at low partial pressures, as in the case of the aqueous MEA, while at high partial pressures the solubility of hydrogen sulphide exceeds that in sulfolane. Thus, in the Sulfinol process, from the standpoint of hydrogen sulphide capacity, the solvent is nearly equivalent to aqueous MEA at very low partial pressures, and is much superior at high partial pressures. The Sulfinol solvent is normally loaded to at least 85 per cent of the equilibrium value for the absorber bottom temperature, and consequently, when treating very sour gases, the solvent circulation requirements may be as little as one half those for aqueous MEA.

The regeneration of a fat solvent is essentially a matter of increasing the equilibrium partial pressure of acid gas over that of the fat solvent by increasing the temperature, then employing pressure reduction and usually a stripping gas such as steam to reduce the acid gas content to the required level. Figure 8 shows the effect of temperature on the equilibrium partial pressure of the Sulfinol solvent and, for comparison, that of aqueous MEA. With the Sulfinol solvent the acid gas equilibria are clearly more sensitive to temperature. From a

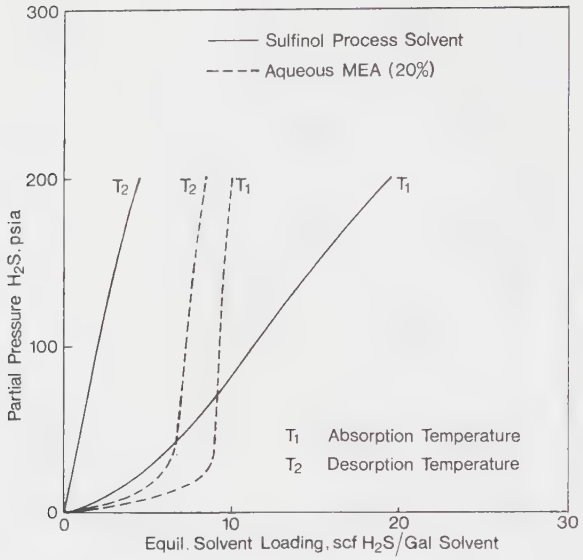


FIG. 8. H_2S absorption—desorption isotherm.

process viewpoint this is reflected directly in a much greater ease of regeneration, i.e. less stripping steam is required per gallon of solvent. Since less solvent needs to be circulated (Fig. 7) the stripping steam requirement per unit of acid gas is strikingly low. The regeneration of solvent relative to mercaptans and carbonyl sulphide is easily achieved during stripping of hydrogen sulphide.

Removal of Objectionable Odours (Sweetening Processes)

The object of sweetening processes is to ensure that the finished products do not have objectionable odours. As a general rule these odours do not materially affect the performance of the product. Hydrogen sulphide, however, in addition to being malodorous, is both toxic and corrosive, and thus affects performance. The objectionable odours are normally attributable to traces of mercaptans, and it is necessary either to remove them by extractive processes or by hydrodesulphurization, or to convert them into innocuous disulphides.

Table IX gives a list of the many processes that have been used to remove objectionable odours; many of them are now obsolete, although it is probable that even these are still used at isolated refineries.

A critical analysis of the then current sweetening processes, sponsored by the API, was made by Happel, Cauley, and Kelly[13] in 1942, but most of the processes have now been superseded. Of these older processes the copper chloride process will be described here in some detail, since it is still used and is typical of the old positive oxidation chemical treating processes. Moreover, many of its fundamentals, and some of its problems, particularly those concerned with feedstock quality, are common to practically all sweetening processes.

The feed preparation in positive oxidation processes must be designed, not

TABLE IX
Removal of Objectionable Odours (Sweetening Processes)

Caustic wash
Doctor treatment
Hypochlorite wash
Solutizer and Dualayer processes
Copper chloride sweetening
Inhibitor sweetening
Sulphuric acid treating
Vapour phase clay treatment
Molecular sieves
Chelate sweetening
Merox process
Mercapfining
Hydrofining/hydrotreating
Lead sulphide sweetening
Unisol treating
Bender-Petreco
Merifining

only with the basic sweetening objective in mind; the effect of the oxidation reaction on other quality characteristics can be quite critical, particularly the stability concerning colour, gum formation, oxidation, and thermal treatment. This is due to the presence in the feed of compounds which have an affinity for oxygen, such as naphthenic acids, phenols, and nitrogen compounds. Such compounds may be present owing to fortuitous contamination and/or incipient cracking in prior processing of the feedstock. They are, however, generally present to some extent in most crudes, and as a consequence, some distillates may suffer a degree of quality deterioration in positive oxidation sweetening processes.

Copper Chloride Process

The copper chloride process is used to sweeten gasolines and kerosines by the direct oxidation of mercaptans to disulphides, using cupric chloride as the oxidizing agent. It has been used in three forms: the liquid, the slurry, and the fixed-bed processes. The first is now very seldom used because of the high corrosivity of the aqueous cupric chloride solution. The other two are still used, and have been extensively reported in the literature.[14,15,16,17,18]

In the fixed-bed process the sour charge is passed through a bed of fullers' earth impregnated with an aqueous solution of cupric chloride; in the slurry process the sour charge is mixed with a slurry of impregnated earth and water. The essential characteristics of both processes are much the same, and the following description concerns the fixed-bed process, a simplified flow diagram of which is given in Fig. 9.

The sour charge is caustic washed to remove traces of hydrogen sulphide which would otherwise deactivate the cupric chloride. It then passes first through a sand coagulator to remove any caustic and/or water haze, and secondly through a rock salt drying tower to ensure complete removal of free

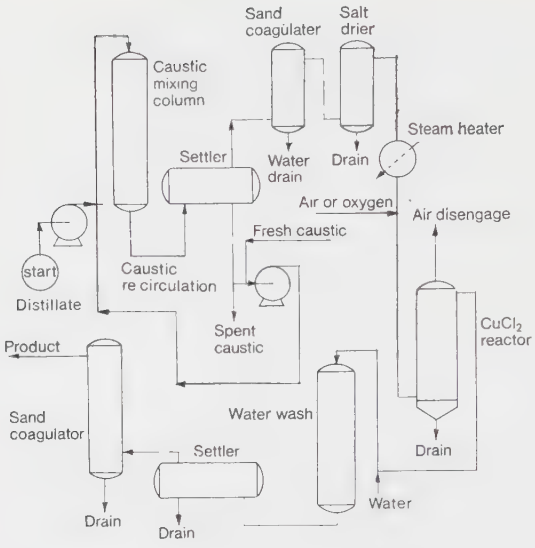


FIG. 9. Fixed-bed copper chloride sweetening.

water, which would adversely affect the water balance in the reactor. After passing through a preheater to raise the temperature sufficiently to dissolve the water formed during the process, air or oxygen is injected into the line, and the dried and oxygenated feed flows upwards through the reactor which contains a bed of fullers' earth impregnated with cupric chloride. The sweetened product is water-washed to remove traces of acidity, clarified from water haze in an upflow sand coagulator, and passed to storage.

The basic reactions of the process may be expressed as follows:

Sweetening

$$\underset{\text{Cupric chloride}}{CuCl_2} + \underset{\text{Mercaptan}}{2RHS} \longrightarrow \underset{\text{Cupric mercaptide}}{Cu(SR)_2} + \underset{\text{Hydrochloric acid}}{2HCl} \quad (1)$$

$$\underset{\text{Cupric mercaptide}}{Cu(SR)_2} + \underset{\text{Cupric chloride}}{CuCl_2} \longrightarrow \underset{\text{Cuprous chloride}}{Cu_2Cl_2} + \underset{\text{Disulphide}}{RSSR} \quad (2)$$

Regeneration

$$\underset{\text{Cuprous chloride}}{Cu_2Cl_2} + \underset{\text{Hydrochloric acid}}{2HCl} \longrightarrow \underset{\text{Chlorocuprous acid}}{Cu_2Cl_22HCl} \quad (3)$$

$$\underset{\text{Cuprochlorous acid}}{Cu_2Cl_22HCl} + \underset{\text{Oxygen}}{\tfrac{1}{2}O_2} \longrightarrow \underset{\text{Cupric chloride}}{2CuCl_2} + \underset{\text{Water}}{H_2O} \quad (4)$$

There is a net production of water, and this must be removed continuously to maintain correct reaction conditions. This is achieved by the aforementioned preheating. Hydrochloric acid is liberated temporarily in the first stage (1),

and is recombined in the regeneration stages (3 and 4). This HCl must not be leached out as it is essential to the regeneration process in which the reaction should be practically instantaneous. This is in order to prevent the cuprous chloride, formed in the second stage of the sweetening process, from having a finite existence during which it would combine with mercaptan to form an oil-soluble cuprous mercaptide which neither reacts in accordance with equation (2) to release disulphide, nor enters into a regeneration reaction with oxygen to reform cupric chloride. Under such circumstances the oil-soluble mercaptide would be removed from the reactor bed to give a sour product of high copper content, leaving behind a deactivated oxidizing agent.

The HCl is also important in that it complexes with the sparingly water-soluble cuprous chloride to form chlorocuprous acid which is soluble in water, and thus permits the regeneration of the cuprous to the cupric salt to take place in the aqueous phase at maximum velocity. The solubility of cuprous chloride in water is also increased by the addition of ammonium chloride.[18,19]

Mercapfining

In mercapfining, as in most other sweetening processes, mercaptans are converted into disulphides which remain dissolved in the product. Conversion is accomplished by oxidation with air in the presence of a fixed-bed catalyst. The process is extremely simple, as shown in Fig. 10.

Sufficient air to sustain the catalytic reaction is injected into the feedstock prior to its entry into the top of the reactor, from the bottom of which the sweetened product emerges. Periodically the catalyst has to be reactivated by passing a regenerating solution over it.

The process is operable over a fairly broad temperature range, and is not greatly affected by pressure, provided that sufficient is maintained to deliver the necessary air. The quantity of air required is dictated by the mercaptan content of the feedstock.

The process has been successfully applied to a variety of feedstocks such as those shown in Table X, and produces sweet products of good quality as shown by the data in Table XI.

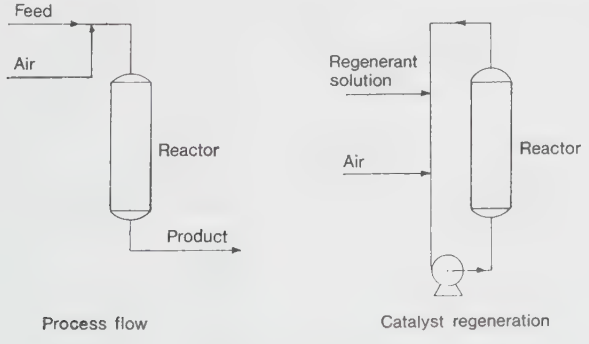


Fig. 10. Mercapfining.

TABLE X
Mercapfining—Typical Feedstocks

	Light catalytic naphtha	Heavy catalytic naphtha	12-pound* catalytic naphtha	Light virgin naphtha	12-pound* virgin naphtha	Re-run naphtha
Distillation, °C						
IPB	44/48	60/77	35/40	38/43	32/46	49
5%	59/66	88/104	41/45	54/60	42/48	71
50%	104/116	177/188	60/66	104/116	65/71	132
90%	154/177	199/216	115/138	143/149	104/127	199
FBP	182/204	216/232	171/188	160/171	138/171	213
Gravity						
°API at 60°F (15.5°C)	59 ± 3	40.5 ± 3	69 ± 3	66 ± 2	75 ± 2	48 ± 4
Sp gr at 15.5/15.5°C	0.743	0.823	0.706	0.716	0.685	0.788
True vapour pressure, psi at 29.4°C	6/6.5	1/3	9/10.5	8/10	9/11.5	6.0
Viscosity, cp at 37.8°C	0.5	0.6	0.5	0.5	0.5	0.6
Average molecular weight	97	135	77	103	80	110
Specific heat at 49°C	0.52	0.49	0.53	0.54	0.55	0.50
Hydrogen sulphide, %wt	0.0010	0.0001	0.0010	0.0003	0.0004	0.0002
Mercaptan sulphide, %wt	0.0050	0.0100	0.0070	0.0030	0.0109	0.0050
Total sulphur, %wt	0.026	0.060	0.020	0.015	0.013	0.020
Phenols, %wt	0.097	0.080	0.050	—	—	—
Thiophenols, %wt	0.005	0.009	0.004	—	—	—

* 12 pounds Reid Vapour Pressure.

TABLE XI
Mercapfining—Product Qualities

	Light catalytic naphtha		Virgin naphtha	
	Raw gasoline	Mercapfined gasoline	Raw gasoline	Mercapfined gasoline
Doctor test	Sour	Sweet	Sour	Sweet
Hydrogen sulphide, %wt	0.0008	None	0.0006	None
Mercaptan sulphide, %wt	0.0035	Nil	0.012	Nil
Total sulphur, %wt	0.027	0.026	0.031	0.029
Phenols, %wt	0.093	0.093	—	—
Thiophenols, %wt	0.005	Nil	—	—
ASTM gum, mg/100 ml	3.1	2.2	0.4	0.2
Copper dish gum, mg/100 ml	9.8	6.7	3.2	2.3
Induction period, minutes	450	610	630	915
°API, 60°F (15.5°C)	61.0	61.0	75	75
Copper strip corrosion	—	1a	—	1a
Saybolt colour	+22	+20	+29	+29
True vapour pressure, psi at 29.4°C	6.0	6.0	9.0	9.0

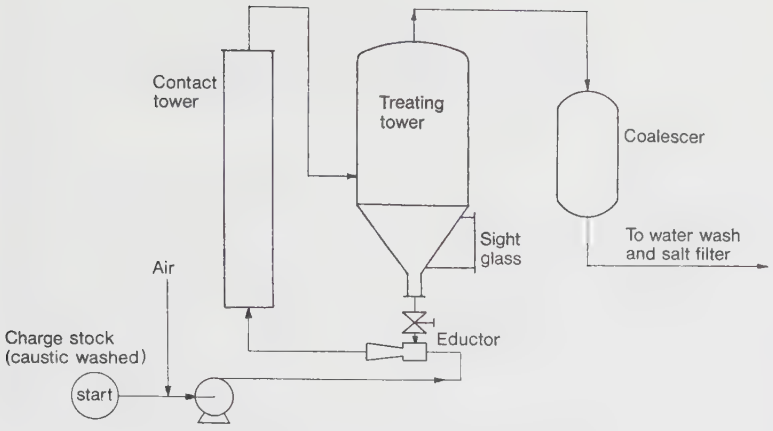


FIG. 11. Chelate sweetening process (Mobil).

Chelate sweetening[21]

Chelate sweetening of gasoline as used by Mobil proceeds in three stages: extraction of the mercaptan by the caustic solution; oxidation of the mercaptan by the oxygen supplied by the chelate; regeneration of the reduced chelate by oxygen (air) present in the in-coming gasoline.

The reaction may be represented by the equations:

$$2RSH + 2NaOH \longrightarrow 2RSNa + 2H_2O$$

$$2RSNa + \tfrac{1}{2}O_2 + H_2O \longrightarrow RSSR + 2NaOH$$

A typical chelate is the reaction product of *NN'*-disalicylidene-1,2-propanediamine (metal deactivator) and cobaltous chloride hexahydrate, dissolved in a caustic soda solution containing cresols to solubilize the chelate.

Figure 11 shows a flow diagram of the process, and typical operating conditions for a pilot plant are given in Table XII. Table XIII shows the main quality characteristics of gasolines treated by the chelate and copper chloride processes.

TABLE XII

Typical Operating Conditions for Chelate Sweetening Pilot Unit

Charge rate, brl/hr	30
Pressures, psig	
Eductor inlet	70–80
Δp across eductor	60 70
Temperature in treater, °C	26–30
Ratio vol. solution/vol. gasoline from eductor	0.1 to 0.15
RSH content, ppm	
Charge	25
Product	Dr. Sweet
Doctor test	
Bottom of contact tower	Slightly positive
Top of contact tower	Negative
Air, cu ft/min	0.08

TABLE XIII
Comparison of Gasoline Quality

Type sweetening	Chelate		Copper chloride
ASTM gum, mg/100 ml			
Total	5.8[1]	4.2[2]	6.2[3]
Pentane washed	1.0	1.0	1.6
5 hr accel. gum, mg/100 ml			
Total	11.5	8.0	12.0
Pentane washed	6.1	4.5	5.3
Induction period, min	470	745	534
ASTM gum increase after 14 weeks storage at 43°C			
Total	2.0	1.0	1.5
Pentane washed	1.8	0.4	0.9

[1] Contains 5 pounds inhibitor A and 1 pound metal deactivator per thousand barrels.
[2] Contains 5 pounds inhibitor B and 1 pound metal deactivator per thousand barrels.
[3] Contains 5 pounds inhibitor A and 3 pounds metal deactivator per thousand barrels.
Inhibitor A: 2,6-di-*tert*-butyl-4-methyl phenol
Inhibitor B: *N*,*N*′-di-*sec*-butyl-*p*-phenylenediamine
Metal deactivator: *N*,*N*′-disalicylidene-1,2-propanediamine

Merox Process[23]

The Merox process developed by Universal Oil Products, is a combination of mercaptan extraction and sweetening. Either process may be carried out independently if desired, in which case the processes are referred to respectively as Merox Extraction and Merox Sweetening. The combined operation is applicable to many jet fuels and kerosines.

Merox extraction (Fig. 12)

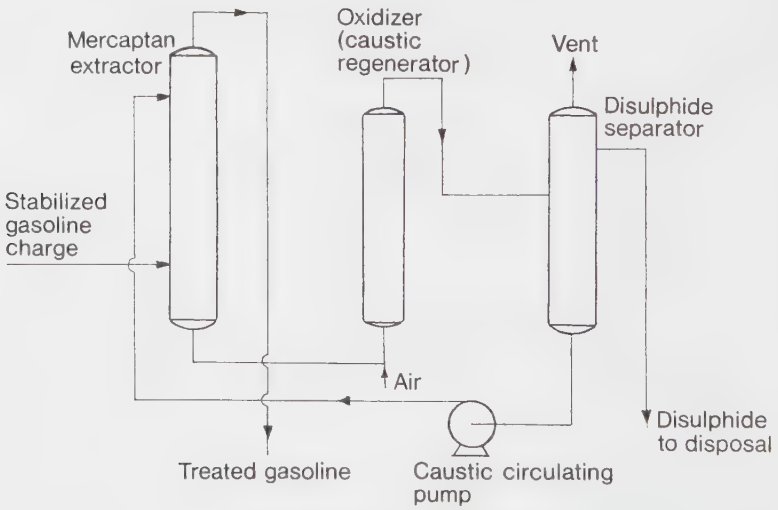


FIG. 12. Merox extraction.

The mercaptans are extracted by an aqueous solution of caustic soda according to the equation:

$$\underset{\text{(oil)}}{RSH} + NaOH \rightleftharpoons \underset{\text{(aqueous)}}{NaSR} + H_2O \qquad (1)$$

Since the reaction is reversible it is impossible to get complete removal of mercaptans by extraction alone without the use of an excessive amount of caustic soda solution. The forward reaction is favoured by low temperature, low molecular weight of the mercaptan, and high caustic concentration. It is also promoted by the use of compounds that increase the solubility of the mercaptan in the aqueous phase.[24,25,26,27] Of these, methanol, as used in the Unisol process, is by far the most effective, but isobutyric acid and cresols have also been used.

The caustic is regenerated, after separation from the hydrocarbons, by blowing with air in the presence of a catalyst at ambient temperature, the reaction proceeding according to the equation:

$$2NaSR + \tfrac{1}{2}O_2 + H_2O \rightleftharpoons RSSR + 2NaOH \qquad (2)$$

The disulphides so formed are insoluble in the caustic soda and are removed in a gravity separator, the caustic being recirculated for further use.

The catalyst, which consists of an iron-group metal chelate, may be in solution in the caustic, in which case the caustic and air are brought into contact in a reactor such as an orifice column, a mechanically stirred reactor, or some other type of gas/liquid contactor. Alternatively, the catalyst may be supported on a carrier, in which case the caustic and air are passed together over a packed bed.

Merox sweetening (Fig. 13)

Sweetening is achieved by blowing a caustic/hydrocarbon mixture with air in the presence of the catalyst, whereby disulphides are formed according to

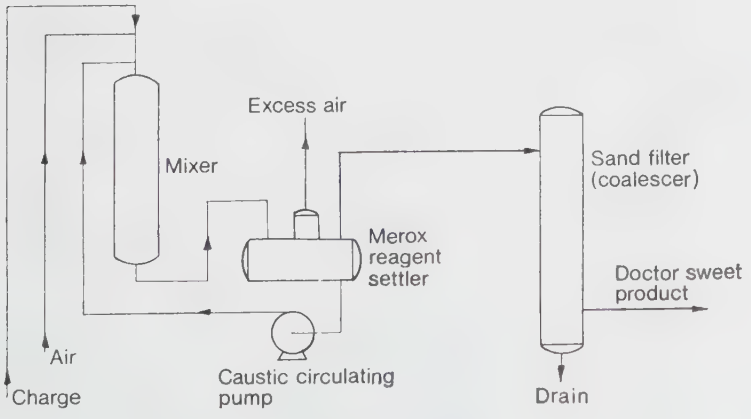


Fig. 13. Merox sweetening.

TABLE XIV

Merox Sweetening of Cracked and Straight-run Gasolines

Sample and crude source	Cat. cracked Wyoming pipeline crude		Visbreaker gaso. Wyoming pipeline crude		Lt. S.R. gasoline Mid-Continent crude			T.C. & S.R. Rocky Mountain crude	
	Raw	Trtd	Raw	Trtd	Raw	Trtd	Trtd	Raw	Trtd
Doctor test	Pos.	Neg.	Pos.	Neg.	Pos.	Neg.		Pos.	Neg.
Mercaptan sulphur, % wt	0.014 4	0.000 2	0.064 4	<0.000 2	0.002 5	<0.000 2	<0.000 2	0.026	0.000 3
Hydrogen sulphide, % wt	0.0	0.0	0.0	0.0	0.0	0.0	—	0.0	0.0
Total sulphur, wt %	—	—	—	—	0.014	—	—	—	—
Induction period (UOP Bomb) min.	85	50	—	—	—	—	—	965*	—
0.002% UOP No. 5 inhib.	—	190	—	—	—	—	—	—	—
0.004% UOP No. 5 inhib.	—	300	—	—	—	—	—	—	—
Gravity, °API, 60°F	60.6	—	68.3	—	75.9	—	—	65.6	—
Distillation, °C									
IBP	43	—	31	—	41	—	—	32	—
10%	59	—	55	—	51	—	—	48	—
50%	96	—	99	—	71	—	—	92	—
90%	145	—	135	—	93	—	—	168	—
FBP	167	—	153	—	114	—	—	199	—
Sweetening Cond.									
Temp, °C	—	40	—	40	—	40	24	—	40
Pressure, psig	—	100	—	100	—	100	100	—	100
Catalyst type	—	dissolved	—	solid	—	solid	solid	—	solid

* As received sample contained caustic-extractable inhibitor.

equation (2), and dissolve in the material being treated. As in the above-mentioned regeneration process, the catalyst may be in solution in the caustic or held on a carrier, and the process is carried out as described.

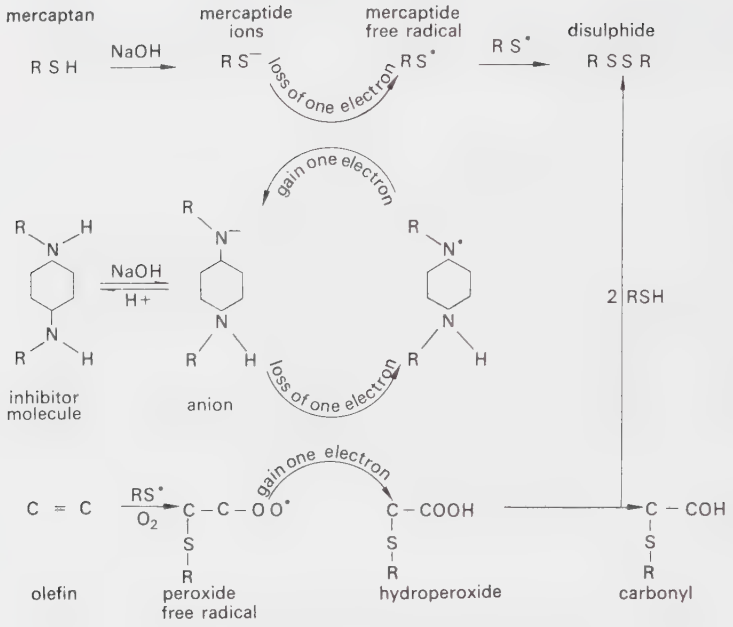
Combined operation

The joint extraction/sweetening operation is carried out by a combination of the operations shown in Figs 12 and 13. Oxygen-free gasoline is fed to the bottom of the vertical extractor and flows upward, counter-current to the downward flow of caustic soda containing the catalyst in solution. Mercaptans are thereby extracted, and the rich caustic from the bottom of the extractor passes to the oxidizer where it is mixed with air. The disulphides so formed are separated from the caustic in the disulphide separator, and regenerated caustic from the separator is recirculated to the top of the extractor. Disulphides are withdrawn from the separator to disposal, and excess air is vented.

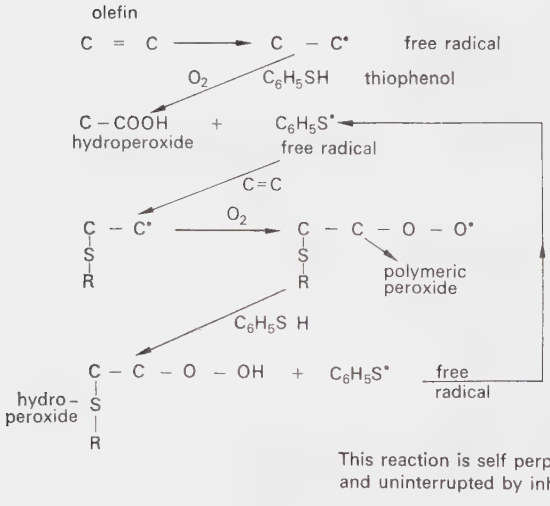
In some applications sufficient mercaptans can be removed by extraction alone without the use of subsequent sweetening. Feed and product quality data are given in Tables XIV and XV.

TABLE XV
Merox Sweetening of Jet Fuels, Kerosine, and Gas Oil

	JP-4 (S.R. naphtha) Wyoming pipeline crude		Kerosine Rocky Mountain crude		Virgin gas oil Gulf Coast sour crude	
Sample and source	Raw	Trtd	Raw	Trtd	Raw	Trtd
Doctor test	Pos.	Neg.	Pos.	Neg.	Pos.	Pos.
Mercaptan sulphur, % wt	0.0220	0.0003	0.0068	0.0003	0.0404	0.008
Colour	25	14	29	19	—	—
Colour after 20 hr at 100°C	23	14	19	19	—	—
Water tolerance test	1	1	—	—	—	—
Thermal stability (CFR coker test)						
ΔP rise after 300 min, in Hg	0.1	1.7	—	—	—	—
Tube rating, max	1	1	—	—	—	—
Gravity, °API, 60°F	54.8	—	42.1	—	37.1	—
Distillation, °C						
IBP	59	—	189	—	218	—
10%	84	—	203	—	229	—
50%	153	—	224	—	252	—
90%	203	—	246	—	302	—
FBP	222	—	260	—	324	—
Sweetening conditions						
Temp., °C		40	—	40	—	47
Pressure, psig		100	—	100	—	100
Catalyst type	—	Solid	—	Solid	—	Solid



(a)



(b)

FIG. 14. (a) Mechanism of inhibitor sweetening, (b) Mechanism of thiophenol interference in inhibitor sweetening.

Inhibitor sweetening

Certain gasoline anti-oxidant inhibitors of the phenylene diamine type are able to sweeten olefinic gasolines containing not too high a concentration of mercaptans, provided there are also present oxygen and a trace of caustic soda left over from caustic washing. The reaction is rather slow and may conveniently take place in the storage tanks. Only a small amount of dissolved oxygen is required, and sufficient may already be present in the gasoline or be introduced during treating operations. If the product is of low vapour pressure, enough air may be introduced into the tank during normal pumping operations.

The process is used chiefly where the necessary storage time for sweetening, usually of the order of a few hours to one day, can readily be made available. The product is usually 'odour-sweet' rather than 'doctor-negative'. The generally accepted mechanism for inhibitor sweetening is shown in Fig. 14(a). An important fact about the process is the need to precede it with a strong caustic wash to remove thiophenol, which is a strong gum precursor. The mechanism for thiophenol interference in inhibitor sweetening is shown in Fig. 14(b).

Merifining[28]

The Merichem Company has developed a range of sweetening processes using a proprietary Fiber-Film bundle to achieve intimate contacting between the hydrocarbon feed and the caustic solution. The Fiber-Film bundle is comprised of long, continuous small-diameter fibres placed in a pipe. The caustic solution preferentially wets the fibres, creating a very large interfacial area. The hydrocarbon stream flows as a continuous phase through the fibre bundle, coming into intimate contact with the caustic adhering to the fibre surface. The treated hydrocarbon contains minimal caustic carry-over limits. Furthermore, the fibre bundles can be installed easily in existing systems. Variations of the process are described below.

Merifining

This process basically uses caustic (15–25°Be) to extract organic acids, mercaptans, and other sulphur compounds from catalytic cracked hydrocarbons. More than one stage of contacting can be used to maximize extraction. The product has better stability and TEL response, because oxidation promoters such as thiophenols are more completely removed.

Napfining

This variation of the process extracts naphthenic and other organic acids from petroleum distillates to produce specification neutralization number in kerosine and jet fuels in a single stage using caustic strength of 5–15°Be, rather than the more usual 3–5°Be, without forming stable emulsions. The stronger caustic results in an aqueous effluent of reduced volume and increased sodium naphthenate concentration, thereby generating a potentially reclaimable by-product.

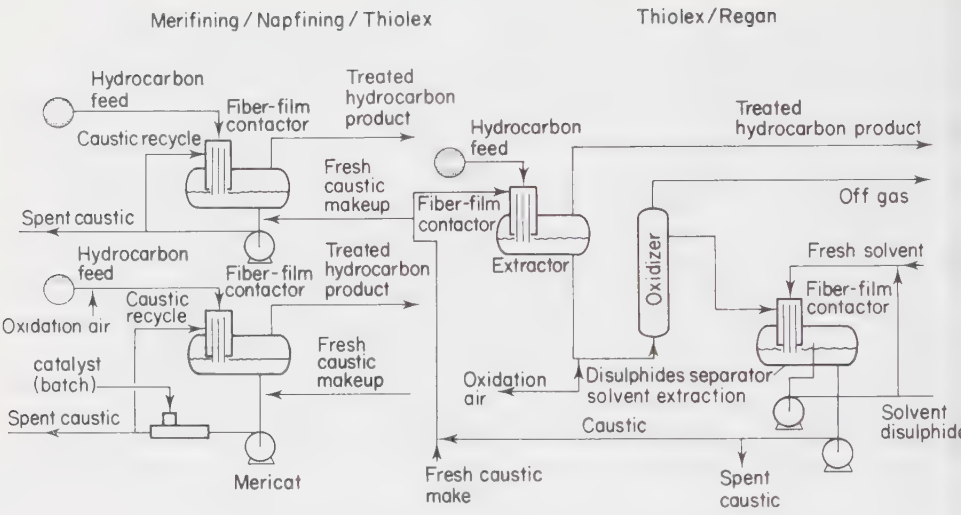


FIG. 15. Merifining. (Courtesy of Merichem Company, USA.)

Mericat

The process uses an oxidation catalyst-bearing caustic solution (10–25°Be) and air to oxidize gasoline mercaptans to disulphides, resulting in a Doctor Sweet product. A wide range of feed mercaptan levels are tolerated.

Thiolex

The application of this modification of the process uses caustic (10–25°Be) to extract hydrogen sulphide and mercaptans from fuel gas, propane, butane, alkylation feed, and straight-run gasolines. The degree of extraction depends on the client's needs. The products are non-corrosive, and gasoline streams have better stability and TEL response.

Hydrofining[29,30,31,32,33]

Hydrofining is the process first introduced by Esso, and a term now given, rather loosely, to different forms of hydrodesulphurization. The process basically is a catalytic sweetening process using mild hydrogenation. The process removes traces of olefins and contaminants that are malodorous or initiate instability. Performance characteristics are improved by a more severe hydrogenation for sulphur removal.

Esso hydrofining has been successfully applied to gas oil, diesel fuel, kerosine, virgin naphtha, solvents, cracked naphtha, heating oil, lubricating oils, and waxes.

The process can be economically attractive even when the required hydrogen must be manufactured. The economics are especially attractive when by-product hydrogen is available from a catalytic reforming unit.

Operating conditions

Because of the many applications of this process, operating conditions vary greatly. Typical operating conditions fall within the range shown in Table XVI. For some purposes, very mild conditions are adequate or preferred. For other purposes, more severe conditions are desirable. The selection of the proper operating conditions often has a major effect on the quality of the product and on the plant investment.

TABLE XVI
Hydrofining Operating Conditions. (Courtesy of Exxon Research, NJ)

Temperature, °F	400 to 800
Pressure, psig	50 to 800
Feed rate, V/hr/V	0.5 to >16
Hydrogen:	
Feed to reactor, SCF/Bbl	up to 3500
Consumption, SCF/Bbl	10 to 700

Catalyst

A number of suitable catalysts are available. In selecting the best catalyst for a specific operation, factors such as feedstock, purpose of treatment, and cost should be considered. The catalysts are capable of regeneration and, depending on operating conditions and other factors, retain their activity for six months to two years.

Process flow

As shown in Fig. 16, the feed enters a coil furnace where, depending on the type of feed and the purpose of treatment, it is heated generally to 550–800°F. The hot feed is mixed with fresh hydrogen-containing gas and is transferred to the top of a reactor. In the reactor, which contains a fixed bed of a regenerable catalyst, the feed is treated with hydrogen at pressures of 50–800 psi.

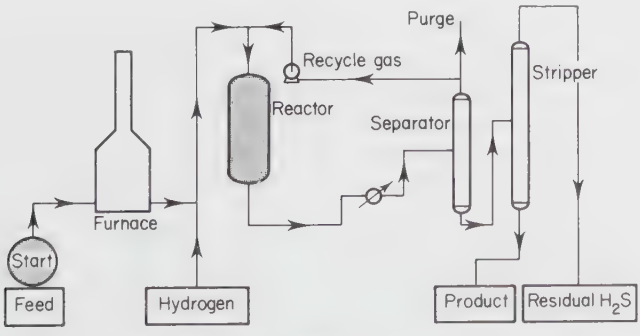


FIG. 16. Esso Hydrofiner. (Courtesy of Exxon Research, NJ.)

After leaving the reactor, the product is cooled and taken to a gas-liquid separator for product and gas separation. If necessary, the hydrogen-rich gas may be recycled back to the reaction zone. After separation, the liquid product enters a stripper where any residual hydrogen sulphide gas is removed.

Feedstocks and product improvement

Naphthas. Hydrofining can be used to improve either virgin or cracked naphthas. For virgin naphthas, the process is most frequently employed to remove sulphur and other catalyst poisons from feedstocks to Power-forming or other platinum-catalyst reforming units. In this application hydrofining serves to improve reforming catalyst activity and life, and to reduce the tendency of the feedstocks to corrode reforming unit equipment. Hydrogen consumption is very low in this service, and the treat gas is often suitable for re-use in hydrofining a heavier distillate stock. Typical results obtained by hydrofining catalytic reformer virgin feedstocks are shown in Table XVII.

TABLE XVII

Hydrofining Virgin Naphtha. (Courtesy of Exxon Research, NJ)

Crude source boiling range, °F	West Texas 200/320		Middle East 200/300	
	Feed	Product	Feed	Product
Sulphur, wt., %	0.12	0.001	0.10	0.001
Mercaptan Number	33.0	0.0	18.0	0.0
F-1 (Research) Octane Number				
Clear	63.5	64.0	48.0	50.0
+2 cc TEL/gal	75.0	81.0	64.0	70.0
Yield, volume per cent		100.0		100.0

In treating cracked naphthas, hydrofining reduces the sulphur content, improves storage stability, prevents the formation of gummy deposits, and corrects the properties that lead to engine fouling. By careful selection of operating conditions, saturation of high octane olefinic components is minimized. Leaded octane numbers remain essentially constant, as shown in Table XVIII.

Solvents. Odour and other quality specifications for solvents used in the dry-cleaning and paint industries are very high. Hydrofining of solvent naphthas under mild conditions improves odour. Even when the source of the naphtha is a sweet crude, hydrofining is often desirable to remove traces of odour. When the source is a sour crude, such as Kuwait, more severe conditions are needed to reduce sulphur as well as to remove other sources of objectionable odours.

Kerosine. Hydrofining can be employed to treat kerosines from either sweet or sour crudes. Hydrofining of kerosines is especially attractive in refineries where sweet crude is not normally available. It effects improvements in sulphur content, odour, colour, and burning qualities (as measured by wick char). The results of hydrofining kerosine are shown in Table XIX.

TABLE XVIII

Hydrofining Cracked Naphthas. (Courtesy of Exxon Research, NJ)

Type of naphtha	Light catalytic		Heavy catalytic		Heavy thermal		Visbreaker	
Boiling range, °F	200/350		270/420		300/450		150/430	
	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Sulphur, wt %	0.18	0.02	0.20	0.14	0.28	0.12	1.00	0.10
Bromine number	71.0	33.0	30.0	27.0	34.0	24.0	50.0	23.0
F-1 (Research) Octane No.								
Clear	88.9	85.9	90.0	90.0	59.5	53.4	71.2	63.6
+2cc TEL/Gal	94.2	93.2	95.0	95.0	70.0	69.8	76.4	75.7
F-2 (Motor) Octane No.								
Clear	77.5	77.5	79.0	79.0	54.7	52.4	66.2	62.4
+2cc TEL/Gal	83.3*	83.3*	84.0	84.0	64.0	63.9	71.8	73.6
Breakdown,								
min. (inhib.)	75.0	375.0	465.0	1 440+	70.0	1 440.0	120.0	1 090.0
G.M. gum (inhib.)	15.0	2.0	3.0	0.5	12.0	0.5	33.0	5.0

* Uninhibited.

TABLE XIX
Hydrofining Kerosine. (Courtesy of Exxon Research, NJ)

Crude source	Mixed Sweet		West Texas	
Boiling range, °F	(340-545)		(310-515)	
	Feed	Product	Feed	Product
Gravity, °API	41.7	42.0	40.6	41.5
Sulphur, wt. %	0.10	0.04	0.55	0.02
Copper number		<1	68	<1
Doctor test		Pass	Fail	Pass
Odour	Fair	Good	Poor	Good
Colour, Saybolt	+20	+28	+3	+24
Colour hold, Saybolt	+18	+26		+21
Wick char	30	18	65	20
Smoke point	22	22	20	20

Heating oils. Hydrofining is well adapted to treating virgin heating oils. Where sulphur is not a problem, adequate sweetening and odour improvement can be attained by very mild conditions, aimed at removing the mercaptans present with minimum hydrogen consumption. If sulphur content is a problem, more severe operations can be employed.

Hydrofining greatly improves the value and quality of cracked heating oils. It reduces carbon deposition while burning, and improves stability and heating-oil pool blending characteristics. On the latter point, experience has shown that carbon residue is a problem when cracked stocks are blended with conversion-sweetened virgin heating oils. Due to an interaction between the converted sulphur compounds in the virgin stock and the unstable components of the crack stock, two stocks of low carbon residue can, when blended, result in a high carbon residue. Hydrofining of the cracked stocks eliminates this problem.

The burning characteristics of typical heating oil blends containing cracked stocks which have been hydrofined are very satisfactory. Burning test results

TABLE XX
Hydrofining Heating Oils. (Courtesy of Exxon Research, NJ)

Feed source	West Texas (Virgin)		West Texas (Virgin)		Catalytic cracking		Thermal cracking	
Boiling Range, °F	330/530		360/655		495/650		300/665	
	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Sulphur, wt. %	0.67	0.47	0.92	0.77	1.4	1.3	1.6	1.2
Copper number	91.0	<1.0	92.0	<1.0	5.0	<1.0	24.0	<1.0
Carbon residue (10% bottoms)	0.07	0.01	0.03	0.02	0.13	0.03	0.40	0.08
Carbon residue Blending value					0.37	0.03	0.49	0.08
Colour, Tag Robinson	24.0	20.0*	17.0	21.0	16.0	18.0	8.0	13.0

* Saybolt colour.

TABLE XXI
Hydrofining Diesel Fuels. (Courtesy of Exxon Research, NJ)

Crude source	West Texas			Elk Basin		83% Virgin Arabian 17% Catalytic stock	
Boiling range, °F	(310-640)			(480-635)		(495-680)	
	Feed	Products		Feed	Product	Feed	Product
Sulphur wt. %	0.92	0.50	0.15	1.3	0.25	1.6	0.35
Copper number	92.0	<1.0	<1.0	34.0	<1.0		<1.0
Gravity, API	37.9	38.4	38.4	31.4	33.5	30.0	32.0
Aniline point, °F	143.0	145.0	150.0	154.0	154.0	151.0	154.0
Diesel index	54.0	56.0	58.0	48.0	52.0	45.0	50.0
Cetane number	←	53–55	→	46.0	46.0	51.0	52.0
Bromine number						10.0	1.0
Colour, Tag Robinson	17.0	18.0	17.0	14.0	22.0		
Carbon residue, (10% bottoms)	0.03	0.01	0.01	0.02	0.02	0.06	0.02

were obtained both in rotary burner operations, where carbon deposition is often critical, and in extended gun-type equipment. The tests were designed to simulate commercial practice. The benefits of hydrofining heating oils are shown in Table XX.

Diesel fuels. With a trend towards a demand for lower sulphur-content diesel fuels, hydrofining permits the use of sour crudes to make quality fuels. It can also be used to upgrade cracked middle-distillate stocks to diesel fuel. Hydrofining of cracked stocks removes sulphur and increases API gravity without any increase in viscosity or pour point. Product improvements realized by hydrofining diesel fuels are shown in Table XXI.

Catalytic cracking feed. Hydrofining can significantly increase the value of either cracked or high-sulphur gas oils for feed to catalytic cracking. For example, product distribution from cracking may be greatly improved, sweetening requirements of cracked products are reduced or eliminated, and the need for scrubbing the catalytic gas stream is avoided. Hydrofining also makes possible cheaper materials of construction for new catalytic cracking units, and reduces equipment corrosion in existing ones.

In addition, total liquid yield from the hydrofining step equals or exceeds 100 volume per cent and, compared with untreated stocks at the same cracking conversion, the hydrofined gas oils produce more naphtha and heating oil, and less carbon, gas, and heavy cycle stocks. The lower carbon yield makes possible the advantages of increased feed rate or higher conversion level.

Typical results for hydrofining catalytic cracking feedstocks are shown in Table XXII.

Processes favoured by other companies are described under the section on hydrodesulphurization.

TABLE XXII

Hydrofining Catalytic Cracking Feed. (Courtesy of Exxon Research, NJ)

Feed	West Texas Gas Oil		
	Raw	Hydrofined	
Inspections			
Gravity, °API	22.3	26.2	
Sulphur, wt. %	2.11	0.22	
Conradson carbon	0.9	0.3	
Nitrogen, wt. %	0.20	0.15	
Nickel, ppm	0.52	0.25	
Vanadium, ppm	1.47	0.42	
Catalytic cracking yields			
Carbon, wt. %	3.2	2.5	3.2
Conversion, vol. %	48.0	48.0	55.0
Dry gas, wt. %	6.1	5.3	6.5
Butanes and butylenes, vol. %	9.7	10.3	15.1
Naphtha, vol. %	38.5	39.4	41.1
Heating oil, vol. %	24.7	26.3	24.5
Cycle stock, vol. %	27.3	25.7	20.5
Catalytic naphtha quality			
Sulphur, wt. %	0.27	0.04	0.04
F-1 (Research) octane no.			
Clear	93.0	93.6	94.3
+3 cc TEL/Gal	97.0	98.4	98.9
F-2 (Motor) octane no.			
Clear	79.5	80.1	80.6
3 cc TEL/Gal	82.6	85.5	86.1
Accelerated storage stability, weeks	1.0	5+	5+

Improvement in Storage Stability

Owing to their complex composition and the presence of small amounts of nitrogen, sulphur, organic acids, and oxygen, most petroleum products are susceptible to deterioration in storage. This storage instability is manifest by a darkening in colour, the formation of gums, and in some cases a significant deterioration in those characteristics that control the performance of the product. Instability may also be accompanied by a marked degree of corrosiveness due to the presence of organic and/or inorganic acids.

Table XXIII lists the means used to control instability, a function which sometimes overlaps that of sweetening to remove malodorous compounds.

TABLE XXIII

Storage Stability Improvements

Caustic extraction
Oxidation inhibitors and metal deactivators
Hydrofining

Caustic extraction

In addition to the use of caustic soda for the removal of acidic gases and malodorous compounds as described earlier, it is widely used for the removal of substances which cause instability and corrosion. The equipment is as described earlier (Fig. 1(*b*)).

Removal of phenols and aryl mercaptans

Gasolines formed by thermal and catalytic cracking contain appreciable quantities of phenols and aryl mercaptans. While some naturally-occurring phenols are useful gum inhibitors, thiophenols and the more reactive alkyl phenols tend to accelerate gum formation. Therefore, it is normal practice to apply prompt and thorough caustic washing to such gasolines as soon as they are produced. The spent caustic cannot readily be regenerated, and because of the malodorous character of thiophenols in particular, disposal in an acceptable manner is a matter of some difficulty.

Removal of fatty acids

Appreciable quantities of formic, acetic, and other low-molecular-weight fatty acids are formed during thermal and catalytic cracking. A water wash usually removes them sufficiently, but where it is necessary to reduce their concentration to very low levels pretreatment with dilute caustic is often applied.

Removal of naphthenic acids

Naphthenic acids, being of fairly high molecular weight, occur only in the kerosine, gas oil, and heavier fractions. Since they are corrosive they must be removed, and since they readily combine with alkalis, their removal from the lighter fractions is not difficult. However, with increasing molecular weight the alkali naphthenate become increasingly soluble in the oil phase, and since they are powerful emulsifiers, separation of the spent alkali from treated oil becomes extremely difficult. The problem may be minimized by using very dilute alkali, even down to 1.5 per cent weight. Alternatively, the addition of low-molecular-weight naphthenic acids to the process increases the solubility of the sodium salts of the heavier naphthenic acids in the aqueous phase, and this diminishes their emulsifying tendency.

Oxidation inhibitor and metal deactivators

It is generally accepted that instability is due to free radical reactions, and Fig. 17 expresses the general view of the chemistry involved. These free radical chain reactions can be terminated by certain inhibitors, some of which are listed in Table XXIV.

The normal practice is to add the appropriate quantity of inhibitor to the product immediately after the mercaptan removal of sweetening processes, on the way to storage.

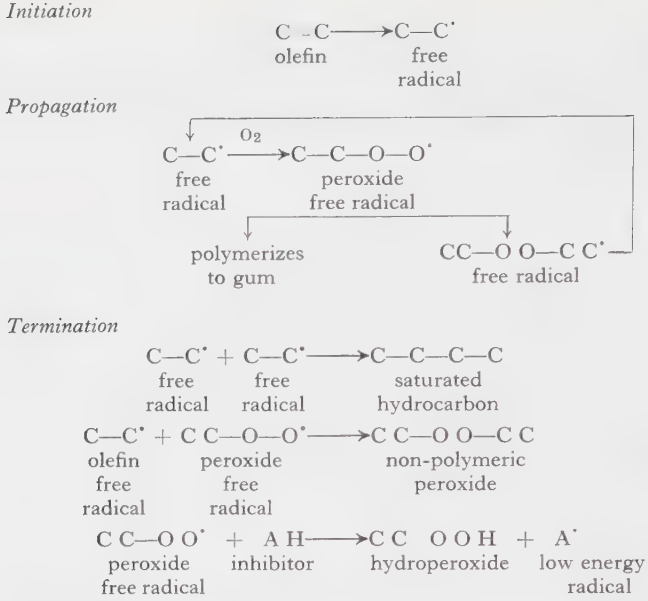


FIG. 17. Mechanism of gum formation and inhibitor action.

Certain metals such as copper can catalyse these chain reactions, and metal deactivator inhibitors are used to prevent this action. The most common of these are the ethylene diamine and propylene diamine derivatives of disalicylidene, also listed in Table XXIV.

Improvement in Performance

The performance characteristics of products from primary refining processes are seldom in keeping with the demands of modern machinery and engines. It is therefore often necessary to subject the product to secondary refining processes to remove those compounds that have an adverse effect on performance. Table XXV lists a number of such processes.

Edeleanu Process

Liquid sulphur dioxide is a very selective solvent for the removal of aromatic hydrocarbons, and is the basis of the Edeleanu process, the oldest solvent extraction process in the petroleum industry.

TABLE XXIV
Instability Inhibitors

Sweetening/Oxidation
*NN'*di-sec-butyl-*p*-phenylene diamine
2,6-Dimethyl-tert-butyl phenol
Metal Deactivators
NN' disalicylidene-1,2-propylene diamine
NN' disalicylidene-1,2-ethylene diamine

TABLE XXV
Performance Improvement Processes

SO_2 extraction (Edeleanu)
Sulfiner acid treating (Howe-Baker)
Hydrodesulphurization (Shell)
Selective hydrogenation (BP)
Udex (Dow/UOP)
Sulfolane extraction

Sulphur dioxide removes aromatics and some polar compounds, including sulphur, gum, and colour constituents, as well as olefins. The process has long been used in the manufacture of premium kerosine, the removal of aromatics leading to considerably enhanced burning properties. It is also used in the refining of lubricating oils, although with heavier feedstocks the solvent power of sulphur dioxide falls to an undesirably low level. The solvent power may be increased by using a mixture of sulphur dioxide and benzene, but selectivity is thereby reduced.

Another disadvantage of the process as applied to lubricating oils is that waxy feedstocks cannot be processed without raising the temperature to the point where excessive pressures would be required to keep the sulphur dioxide liquid. Sometimes the extract rather than the raffinate may be desired, as when gasolines and naphthas are processed for the separation of very high aromatic content fractions.

Operating conditions vary from $-30°C$ for kerosines and other light stocks to $+15°C$ or higher for high pour point materials. The high solvent power and selectivity of sulphur dioxide permit solvent ratios to be kept in the order of 0.5 to 1.5 volumes of solvent per volume of oil, and the number of extraction stages at 2 to 5. Emulsion difficulties are rarely encountered. The flow diagram of a typical plant to process the lighter distillates is shown in Fig. 18. The charge is first dried before passing to the packed extraction tower, since otherwise severe corrosion of equipment would be caused by water in the sulphur dioxide.

The extractor operates at a pressure of about 170 psig, and recovery of sulphur dioxide is effected by flashing at reduced pressure, the final flash taking place under high vacuum.

To improve thermal economy multiple effect evaporation is used in the recovery of sulphur dioxide from the extract. In the sulphur dioxide circuit there is a small drying tower for the continual removal of water, and this is the only piece of equipment that has to be made of corrosion-resistant material.

Sulphuric acid treatment

Many chemical reactions take place when hydrocarbon oils are reacted with sulphuric acid. By appropriate selection of the conditions a variety of refining effects can be achieved to give improvement in colour stability and sweetening. In particular it reacts with many of the unstable and undesired constituents in petroleum fractions, such as sulphur compounds. The early recognition of this, combined with its low cost and ready availability, made it one of the first materials to be used for refining petroleum products.

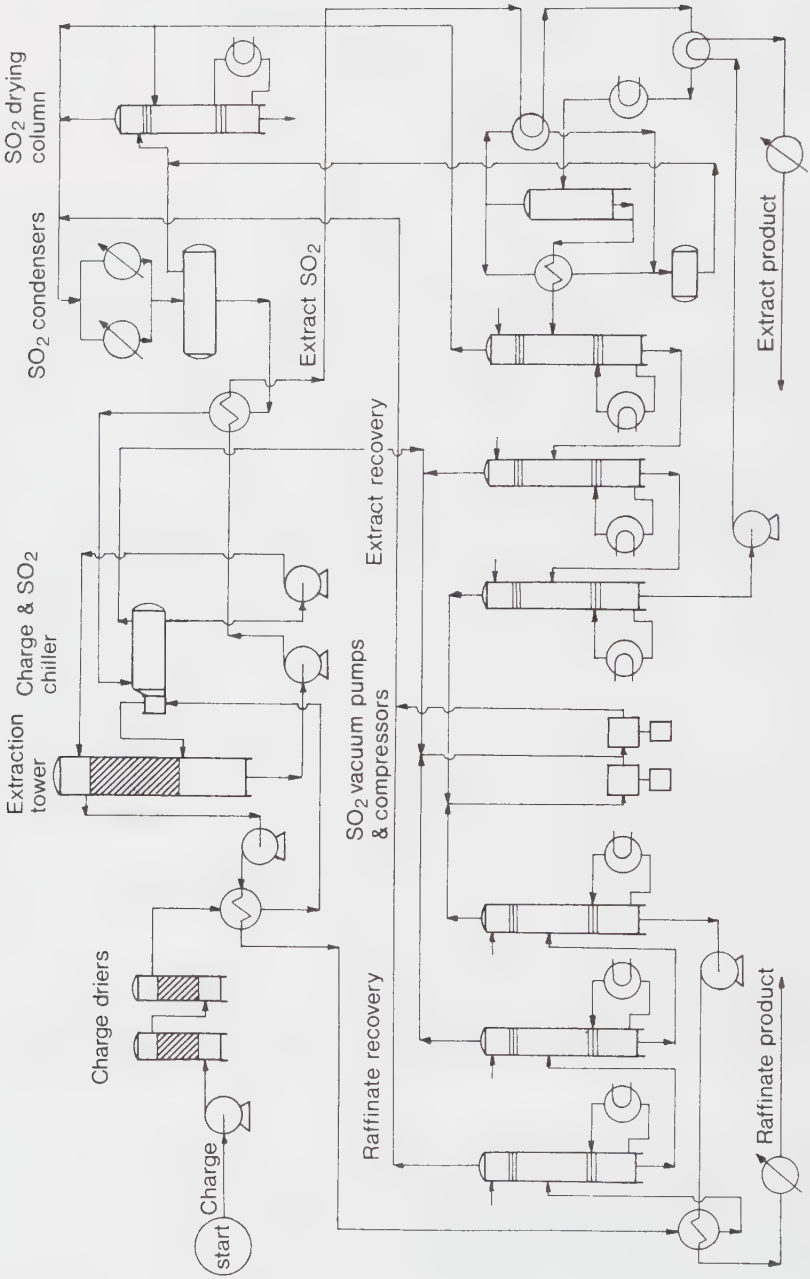


FIG. 18. Edeleanu process.

For many years its versatility put sulphuric acid in the forefront of refining chemicals. However, in recent years its use has steadily declined as other treating methods have been devised. These not only effect a greater improvement in product quality, but do not suffer from the two major drawbacks of acid treatment, the appreciable material loss resulting from the formation of acid sludge and the problem of sludge disposal.

The Howe-Baker Sulfining process is a modern version of the sulphuric acid treating processes for the removal of sulphur and other compounds.

The Howe-Baker process is usually applied to light petroleum distillates. The process uses sulphuric acid in combination with electrostatic mixing to achieve sulphur removal efficiencies in excess of 90 per cent. The process is applicable to the pretreatment of straight-run naphthas that are to be reformed, and for the removal of thiophene from aromatic streams.

Hydrodesulphurization

Hydrodesulphurization, a more severe version of hydrofining, described earlier, is the most modern and most effective process for removing sulphur from oil products, and for a general improvement in the quality of refinery streams, including the pretreatment of catalytic reformer feed.

The process converts sulphur into hydrogen sulphide by reaction with hydrogen in the presence of a catalyst. Many major oil companies have developed their own versions of the process. The fundamentals of all these processes are the same.

Shell Hydrotreating Process

Hydrotreating is an economic and effective process for improving the general quality of petroleum products.

There are two versions of the Shell process, the Shell vapour phase process for light straight-run and cracked fractions, and the Shell trickle flow (liquid phase) process for kerosine and heavier straight-run and cracked distillates up to vacuum gas oil. Both processes employ the same basic line-up, which is shown in Fig. 19. The liquid feedstock is mixed with hydrogen-rich make-up gas and recycle gas. The mixture is heated up to reaction temperature by heat exchange with the reactor effluent and a furnace, and enters a downflow, fixed-bed reactor containing an appropriate catalyst. In the reactor the sulphur and nitrogen compounds present in the feedstock are converted into hydrogen sulphide and ammonia, respectively, and the olefins present are saturated with hydrogen. The typical operating conditions for the process are given in Table XXVI.

The reaction products leave the reactor and, after having been cooled to a low temperature, typically 40–50 °C, enter a gas separator system for liquid separation. The hydrogen-rich gas from the high-pressure separation is recycled to combine with the feedstock, and the low-pressure hydrogen sulphide-rich gas is sent to a gas treating unit where hydrogen sulphide is removed, making the gas suitable as fuel for the refinery furnaces. The liquid stream leaving the low-pressure separation is the product from hydrotreating. It is normally sent to a stripping column where H_2S and other dissolved gases

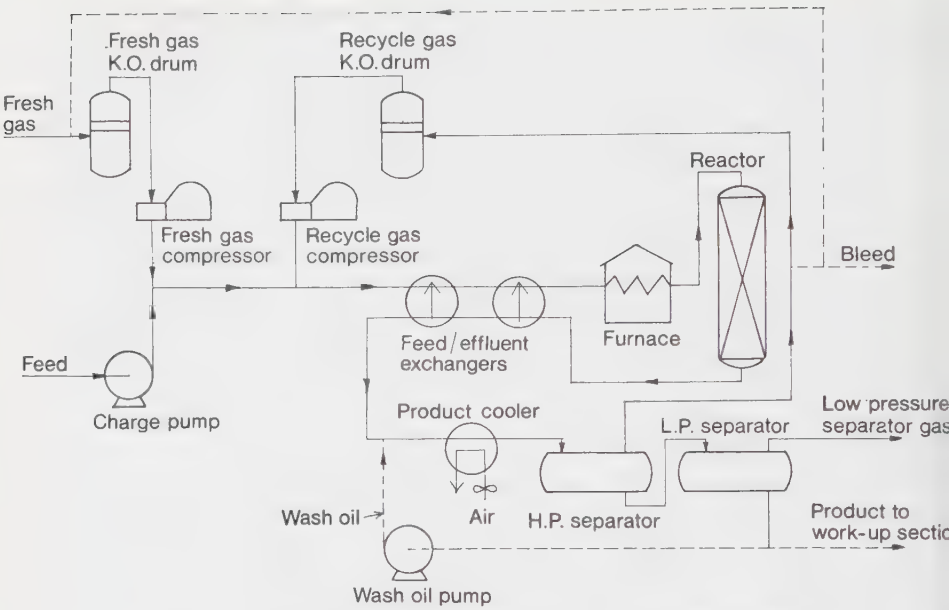


FIG. 19. The Shell vapour phase or trickle flow hydrotreating process.

are removed and finally, in cases where steam is used for stripping, the product is sent to a vacuum drier for the removal of water. The typical utility consumptions for various feedstocks are given in Table XXVII. Alternatively, a four-separator system can be used to provide hot feed to the stripping column, thereby improving energy conservation.

The catalyst used for sulphur removal is usually cobalt and molybdenum finely distributed on alumina extrudates. A nickel/molybdenum-containing catalyst has also been developed for applications where denitrification is the predominant reaction required or where a high degree of saturation is necessary.

Catalysts can normally be regenerated *in situ* by using nitrogen/air, as well as steam/air mixtures. Regeneration *ex situ* is growing in popularity, due to reduced turn-round, improved catalyst regeneration, and less risk to process equipment, especially the recycle gas compressor.

TABLE XXVI

Shell Hydrotreating Processes: Typical Operating Conditions

	Shell trickle flow hydrotreating process	Shell vapour phase hydrotreating process
Space velocity, ton feed/M_3 catalyst/h	0.5–4	2–4
Reactor temperature, °C	330 400	320–380
Gas recycle rate, Nm^3/mt feed	50 300	100–300
Operating pressure, bars	40 100	20–40

TABLE XXVII

Shell Hydrotreating Processes: Typical Utility Consumptions per Ton Intake (Reactor Sections Only)

Feedstock	Full range 250°C	Full range 350°C	S.R. gas oil	L.C.C. C.O.	Flashed distillate	Cat. reformer feed	S.R. kerosine	Thermally cracked gas oil
Process	Shell vapour phase	Shell trickle flow	Shell trickle flow	Shell trickle flow	Shell trickle flow	Shell vapour phase	Shell trickle flow	Shell trickle flow
Consumptions								
Fuel tcals (70% efficiency)	85	65	65	30	70	75	65	55
Electricity, kWh	3.1	10.2	8.0	21.9	15.0	4.8	3.8	14.1
Hydrogen, kg	1.4	1.8	2.8	9.2	4.9	1.1	1.3	7.7
Sulphur % wt feed	0.13	0.65	1.5	2.2	1.8	0.15	0.24	2.5
Product	0.01	0.05	0.2	0.4	0.54	0.000 1	0.01	0.2

The process is extensively used to reduce the sulphur content of refinery streams to make them suitable as finished products or as blending components. It is also widely applied to reduce the sulphur and nitrogen content in the catalytic reformer feed to less than 1 ppm requirement. Other properties like storage and thermal stability, smoke point, cetane number, and density can also be improved by the process. Another interesting application of hydrotreating is the pretreatment of feedstock for catalytic cracking units. By using a suitable hydrogenation-promoting catalyst at severe operation conditions, hydrogen is taken up by the aromatic molecules. The increased hydrogen content of the feedstock obtained by this treatment results in a significant conversion advantage in subsequent catalytic cracking, and higher yields of light products can be achieved.

Shell Smoke Point Improvement Process

The smoke point of kerosine is an important burning characteristic. Kerosine may be broadly classified as paraffins, naphthenes, and aromatics. Of these, paraffins have the least tendency towards smoke formation and aromatics the greatest. Naphthenes are intermediate between the other two. Hence a good quality kerosine must contain a sufficiently high proportion of paraffinic hydrocarbons relative to aromatics.

By hydrotreatment of a kerosine fraction, aromatics can be converted into naphthenes, thereby producing an improvement of burning characteristics. For this purpose the Shell smoke point improvement (SPI) process can be applied. This process closely resembles the conventional hydrotreating unit in line-up. The simplified flow scheme is shown in Fig. 20. In the reactor an aromatics hydrogenation catalyst consisting of a noble metal on a special carrier is used. The typical operating conditions are given in Table XXVIII, and the typical feed/product characteristics and utility consumptions are given in Tables XXIX and XXX. To restrict temperature rise due to the highly

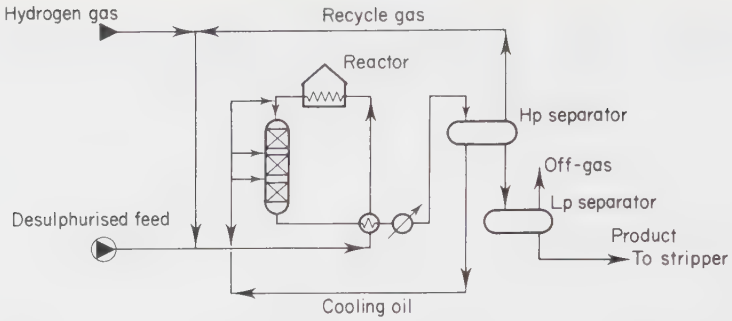


FIG. 20. The Shell smoke point improvement process. (Courtesy of Shell Research, The Hague.)

exothermic aromatics saturation reactions, quench oil from the high-pressure separator is applied between the catalyst beds. The catalyst used is very sensitive to traces of sulphur and nitrogen. Therefore, the feedstock is normally pretreated in a conventional hydrotreater before it is fed to an SPI unit.

TABLE XXVIII
Shell Smoke Point Improvement Process: Typical Operating Conditions

Pressure, bars	50 70
Temperature, °C	230 300
Space velocity, t/m^3h	2.0–3.5
Total gas rate, Nm^3/ton	200 300

Shell Pyrolysis Gasoline Hydrotreating Process

Pyrolysis gasoline (or pygas) is a by-product from the manufacture of ethylene by steam cracking of hydrocarbon fractions such as naphtha or gas oil. Since the yield is typically some 70–80 per cent of the ethylene production, it is a contributory factor in the economics of ethylene manufacture. Pygas is normally produced from the ethylene plant fractionator as a C_5–180/205°C cut.

Traditionally, the outlet for pygas has been into motor gasoline (mogas) blending, a suitable route in view of its high octane number. Only small proportions, however, can be blended untreated owing to the unacceptable

TABLE XXIX
Shell Smoke Point Improvement Process: Typical Feed/Product Characteristics

	Feed	Product
Refractive index, n_d20	1.4430	1.4340
Spec. gravity, 15/4°C	0.800	0.790
Smoke point, mm	20	31
Aromatics, vol. %	17	1.5

TABLE XXX

Shell Smoke Point Improvement Process: Typical Utilities Consumption per Ton Intake (Reactor Sections Only)

Electricity	kWh	30
Fuel	kg	5
Hydrogen	kg	10

odour, colour, and gum-forming tendencies of this material. The quality of pygas can be satisfactorily improved by hydrotreating, whereby conversion of di-olefins into mono-olefins provides an acceptable product for mogas blending.

An alternative objective is the recovery of chemicals such as benzene, toluene, and xylenes (BTX), and production of feedstocks for isomerization units. For this reason two different processes, first- and second-stage pygas hydrotreating, are applied, either separately or integrated.

The purpose of the first-stage hydrotreater (FSHT) is to hydrogenate di-olefins selectively to mono-olefins and thus improve mogas quality, or to produce feedstock for a second-stage unit. The process operates under trickle flow conditions employing high pressures and low reactor temperatures. A specially developed nickel-containing catalyst is used. Liquid product recycle is applied to limit the temperature rise within the reactor. In the FSHT no desulphurization occurs.

A second-stage hydrotreated SSHT is used if the objective is to produce BTX. In this case the product from a FSHT is further treated in a SSHT to saturate the olefins present and to produce an almost completely desulphurized product meeting the stringent olefin and sulphur specifications. Such a SSHT is normally integrated with a FSHT, and a simplified flow diagram of a two-stage integrated unit is given in Fig. 21. The SSHT reactor operates at a higher temperature and at pressure levels similar to the FSHT. It is usually trickle flow at reactor inlet and vapour phase at the outlet. A nickel/molybdenum catalyst on an extrudate carrier is generally used. Again, liquid recycle may be applied. Cool high-pressure separator liquid may also be injected into the reactor between the catalyst beds to control the temperature rise.

The typical operating conditions and feed/product characteristics are given in Tables XXXI and XXXII, respectively.

TABLE XXXI

Shell Pyrolysis Gasoline Hydrotreating Process: Typical Operating Conditions

	FSHT	SSHT
Temperature, °C	80–130	230–380
Pressure, bars	60	45–65
Recycle liquid : feed ratio	3–5	0–2
Space velocity, t fresh feed/M^3 cat/hr	0.8–1.5	1–3
H_2 make-up, NM^3/t fresh feed	50–100	50–125
Recycle gas, NM^3/t fresh feed	200–500	450–1 200

TABLE XXXII

The Shell Pyrolysis Gasoline Hydrotreating Process: Typical Feed/Product Characteristics

	Feed	Product	Feed	Product
Type	C_5–200°C		C_6–200°C	
Maleic anhydride value, mg/g	100–250	5–15	5–15	0
Bromine number, g/100 mg	60–100	25–80	25–80	1
Sulphur content, ppm wt	100–400	100–400	100–400	0.5

Heavy Oil Hydrodesulphurization

Esso/Union GO-FINING

Desulphurization of heavy oils to meet rapidly increasing low sulphur fuel oil markets is one of the major technical and economic challenges facing the refining industry during this decade. One route to low-sulphur fuel oil production is vacuum gas oil desulphurization. Atmospheric residuum is first

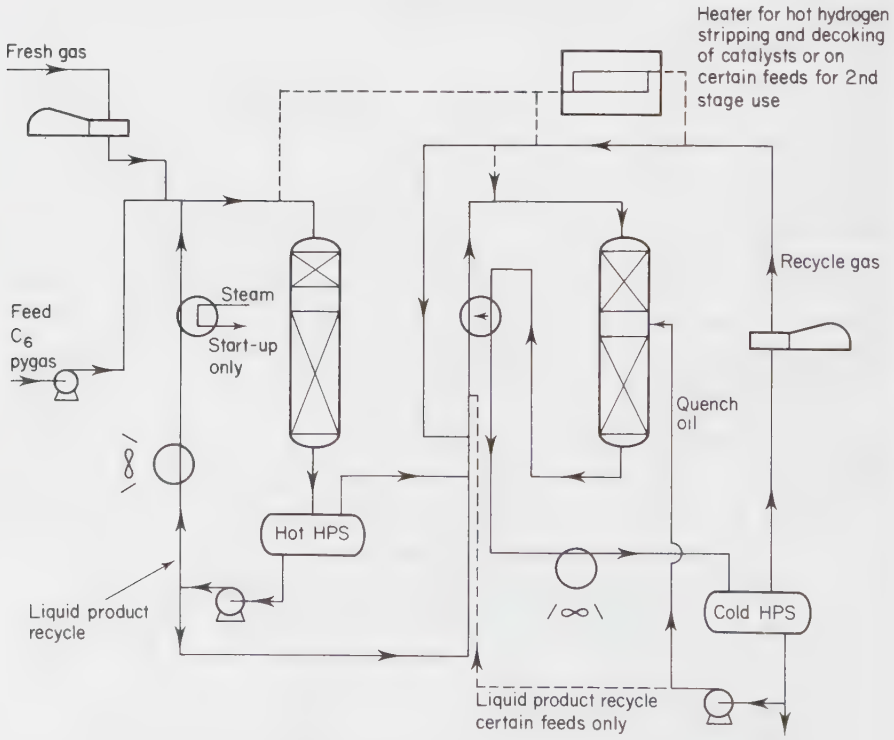


FIG. 21. Typical flow scheme of a Shell integrated first- and second-stage C_{6+} pygas hydrotreater. (Courtesy of Shell Research, The Hague.)

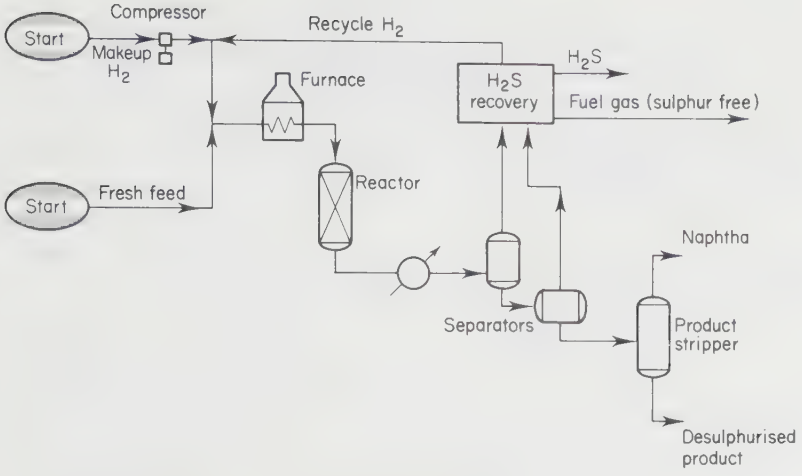


FIG. 22. GO-FINING—simplified flow diagram. (Courtesy of Exxon Research, NJ.)

fractionated in a vacuum distillation tower into a vacuum gas oil and residuum. The sulphur content of the vacuum gas oil is then significantly reduced by means of catalytic hydrodesulphurization. The desulphurized vacuum gas oil can be blended with other fuel oil components to meet the desired fuel oil pool sulphur level. This process has the advantage of being relatively inexpensive. Feedstocks to this process may include virgin and visbreaker vacuum gas oils, thermal and catalytic cycle oils, and coker gas oils. Residua and other heavier feedstocks are hydrodesulphurized in the RESIDIFINING process, described later.

A simplified flow diagram of a Go-finer is shown in Fig. 22. The feed is mixed with treat gas and preheated prior to entering the fixed-bed reactor. Reactor pressures have typically been about 800 psig, but can now be lowered for most feeds. The desulphurized product from the reactor is cooled and enters a high-pressure separator. In this separator a hydrogen-rich stream is recovered which, after scrubbing to remove H_2S and NH_3, is combined with make-up hydrogen to provide the required treat gas for the process. The bottoms stream from the high-pressure separator is subsequently stripped or fractionated to remove remaining gases and a small quantity of naphtha. The product is then suitable for direct blending into the fuel oil pool.

Factors contributing to the operating cost for VGO desulphurization are shown in Table XXXIII. Low-pressure operation reduces the hydrogen consumption as indicated in Fig. 23.

Selective Hydrogenation Process

In recent years there has been a spectacular expansion in the manufacture of ethylene by the pyrolysis of hydrocarbons. The steam cracking of liquid feedstocks for the production of ethylene gives rise to substantial quantities (15–30 per cent on feed) of by-product gasoline containing a high proportion of di-olefins and unsaturated aromatics such as styrene. The gasoline has a high

TABLE XXXIII

Hydrogen is a Major Cost in 800 psig VGO Desulphurization

Operating costs	*Per cent of total cost*
Investment related*	42
Hydrogen†	52
Catalyst and utilities	6
	100%
Investment	*Per cent of total investment*
GO-FINER	37
Offsites and utilities	36
Vacuum pipe-still	27
	100%

* Includes 9 per cent DCF return.
† Hydrogen cost is 60¢/MSCF.

octane number, usually greater than 95, but has poor oxidation and gum stability owing to the di-olefin content. This can be remedied by selective catalytic hydrogenation.

The BP selective hydrogenation process can hydrogenate di-olefins to mono-olefins without saturation of the mono-olefins or the aromatics, and has been in use for some twenty years for the production of gum-stable motor gasolines from steam cracker gasoline. During that time, however, cracking severity has increased from a yield of 15–18 per cent weight in earlier units to about 30 per cent in modern units, as a consequence of which the gasoline by-product now requires over 400 scf/brl hydrogen absorption instead of the earlier

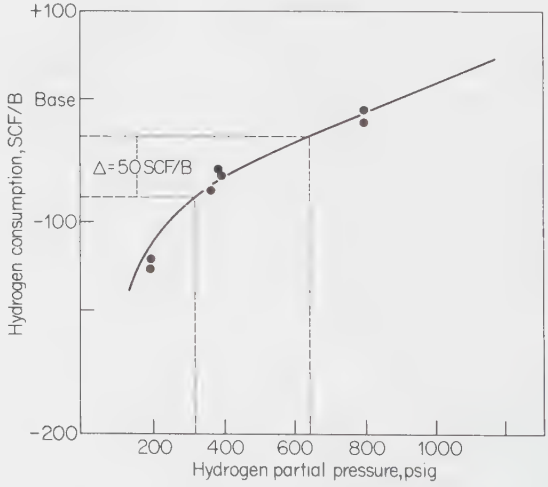


Fig. 23. Lower pressure results in lower hydrogen consumption Agha Jari 90 per cent HDS. (Courtesy of Exxon Research, NJ.)

120–200 scf/brl. Modification in the design of the process has, however, enabled it to treat these gasolines satisfactorily.

Concomitant with these developments there has been an increased need to extract aromatics from steam-cracked gasoline, partly because of the greater size of ethylene units, partly because of the necessity to dispose of large quantities of by-product gasoline, and partly because the higher content of aromatics in gasolines from high-severity cracking made aromatic extraction economically more attractive.

Consequently the BP selective hydrogenation process is now applied more often for the production of aromatics than for the production of stabilized motor gasoline. The usual route for aromatic production is:

(a) Selective hydrogenation to remove di-olefins.
(b) Distillation to give an aromatic concentrate.
(c) Complete saturation of mono-olefins and desulphurization of the concentrate.
(d) Purification of the aromatics by solvent extraction, extractive distillation, etc.

Stages (a) to (c) are illustrated in Fig. 24. Raw steam-cracked gasoline and make-up hydrogen (by-product from the steam cracker) are preheated together by exchange with reactor effluent and pass downflow over the catalyst where the di-olefins are selectively hydrogenated to mono-olefins. The reactor

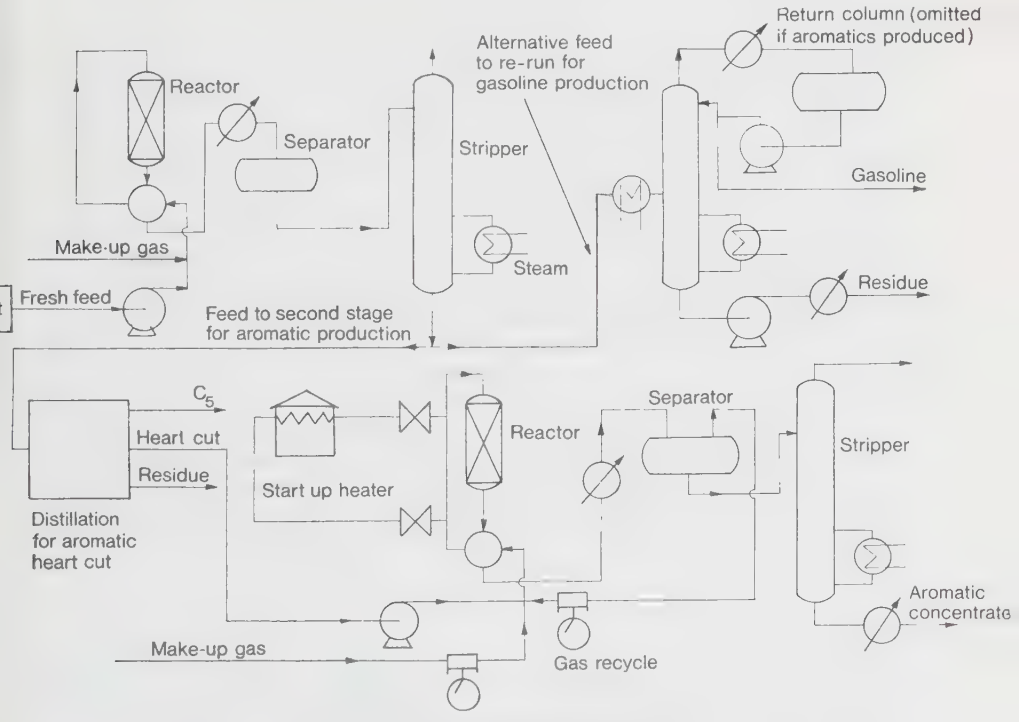


FIG. 24. BP selective hydrogenation process.

TABLE XXXIV

BP Selective Hydrogenation Process: First Stage. Typical Data on Feed and Product. (Courtesy of BP Research, UK)

Typical yields	% wt on feed	
Finished gasoline	96	
Residue	3.5	
Stabilizer gas	0.5	
Product quality	Feed*	Product*
Gravity, °API at 60°F	50.8	52.3
Distillation, °C		
IBP	35	39
10%	52	55
50%	86	83
90%	158	146
FBP	187	190
Bromine number	67	52
Diene number	26	1.5
Total sulphur, % wt	0.012	0.011
Total aromatics, % wt (GLC)	59	59.8
Gum existent, mg/100 ml	20	1
Gum accel (120 min), mg/100 ml	40	2
ASTM induction period, min	175	480
Research ON, clear	96.5	95.0
+3.0 ml TEL/US gal	99.6	100.8

* Inhibited with phenylene diamine anti-oxidant.

product is cooled and excess gas (hydrogen and methane) is taken off from the separator and used as make-up gas. Dissolved gases are removed in a simple stripper, the bottoms from which are either distilled in the re-run column to remove traces of gum, if motor gasoline is the desired product, or distilled to give an aromatic heart cut.

In the second hydrogenation stage, the aromatic heart cut and hydrogen (make-up gas and recycle) are preheated in a feed/effluent heat exchanger and fed to the top of the reactor, and pass downflow over the catalyst where the olefins are hydrogenated and sulphur compounds broken down to hydrogen sulphide. The reaction product is cooled and hydrogen is recycled, a simple stripper being used to remove dissolved hydrogen, methane, and hydrogen sulphide from the product. Typical data on feed and product when operating the first hydrogenation stage for motor gasoline are given in Table XXXIV.

Table XXXV gives typical feed and product analyses for a second-stage hydrogenation in which the feed was a C_6 heart cut containing about 80 per cent benzene, obtained by distillation of a steam cracker gasoline after removal of di-olefins.

Udex Process

The Dow Chemical Company discovered that a concentrated aqueous solution of certain glycols was an excellent selective solvent for aromatics, and from this the Universal Oil Products Company developed their Udex process for the

TABLE XXXV

BP Selective Hydrogenation Process: Second Stage. Typical Analyses of Feed and Product. (Courtesy of BP Research, UK)

Composition	Feed	Product
Benzene, % wt	78.8	78.2
Cyclo C_6, % wt	3.4	3.9
Other non-aromatics, % wt	17.8	17.9
Bromine number	15.5	0.1
Sulphur, ppm	13	1

extraction of benzene, toluene, ethyl benzene, xylenes, and heavier aromatics from gasoline and naphtha fractions.

The process can handle a wide-boiling feed, although for the economic attainment of high purity and high yield it is better to limit the operation to aromatics falling within not more than two adjacent molecular weight brackets. High solvent ratios are used, but operation costs are not excessive because it is the extract that is distilled from the solvent, and not the reverse. A simplified flow sheet of the process is shown in Fig. 25.

Extraction takes place in a column fitted with trays, and at a moderate pressure that permits a fraction rich in the lighter raffinate components to be flashed off from the extract on its way to the stripper, since the latter is operated at atmospheric pressure. This light raffinate fraction is recycled to the extractor in order to reduce the extraction of heavy paraffins which would interfere with

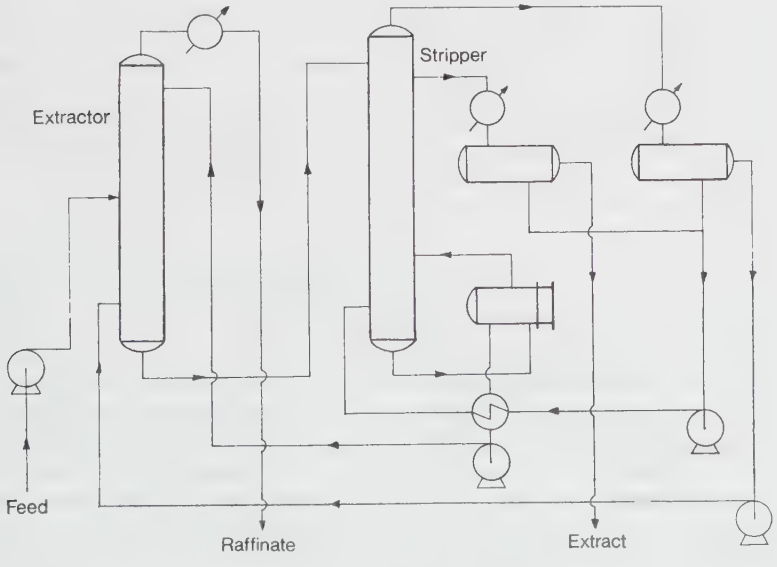


Fig. 25. The Udex process.

the subsequent production of highly pure aromatics; it also serves as a back-washing operation to improve selectivity.

Aromatics are recovered as a wide cut from the stripper, which is equipped with bubble-cap trays and a steam-heated reboiler. The presence of the glycol allows extractive distillation to be used to widen the effective difference in boiling points between paraffins and aromatics. Very pure aromatics are thus obtained, the rejected paraffins being driven overhead as vapour to join the aforementioned light raffinate fraction. Efficient recovery of solvent from both the raffinate and extract streams is easily achieved by water washing.

If the aromatics are to meet specifications for nitration grade, a hot clay after-treat is usually given for the removal of traces of olefins and sulphur compounds.

The Universal Oil Products Company has combined the Udex process with its Platforming process in an operation called Rexforming. The naphtha feed is first Platformed and then extracted for aromatics in a Udex plant. The highly paraffinic raffinate from the Udex plant is recycled to the Platformer. A good yield of highly aromatic and very high octane motor gasoline is obtained by the process.

Shell Sulfolane Extraction Process

The Shell Sulfolane extraction process uses sulfolane (1,1-dioxythiacyclopentane) as the solvent for the extraction of aromatics from hydrocarbon mixtures. The process is used mainly for the manufacture of nitration-grade aromatics (benzene, toluene, xylenes) starting from catalytic reformate or hydrogenated pyrolysis gasoline. It is also used for the extraction of straight-run naphtha or catalytic reformate for the production of low aromatic content hydrocarbon solvents, and for the extraction of kerosine to produce low aromatic content, high smoke point kerosine.

The process can handle a large variety of feedstocks, but to get the best results it is generally advisable to limit the boiling range of the feedstock to a range of three to four molecular weight brackets.

A diagram of the process is given in Fig. 26. The feed is contacted counter-currently with the solvent in a rotating disc contactor, or other contactor, in which the pressure is maintained so that all streams remain liquid. From the top of the extractor a paraffinic raffinate is obtained, containing a small amount of dissolved sulfolane, which is removed in a subsequent water wash. The bottom stream contains all the aromatics plus some, mainly low-boiling, non-aromatics, and is fed to the stripper where the more volatile non-aromatics are distilled off together with some light aromatics.

The overhead stream, after condensation, is recycled to the extractor to recover the aromatics; it is normally introduced at a point below the feed inlet so that heavy non-aromatics, which are difficult to remove in the stripper, are washed out in the bottom section of the extractor. The solvent/aromatic mixture obtained as bottom product from the stripper is separated in the solvent recovery column, which is operated under vacuum. The pure solvent is returned to the extractor via a heat exchanger to reduce the temperature to the required extraction temperature. The top product of the recovery column is freed from sulfolane by applying reflux.

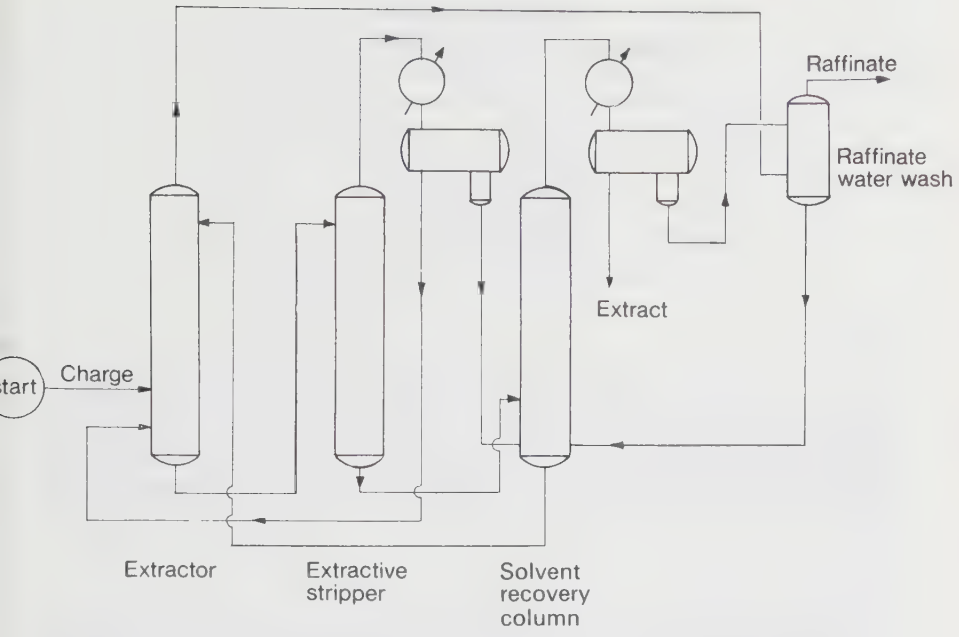


FIG. 26. Shell Sulfolane extraction process.

The extract may be fed directly to the clay-treating step, which is normally required to meet product specifications. The water phase contains only a small amount of sulfolane and can be used as wash medium for the raffinate. The spent wash water is returned to the bottom of the recovery column, to serve as stripping steam.

High yields of very pure aromatics can be obtained by the process. As the solvent is heavier than the feed high solvent ratios can be used with virtually no increase in operating costs, the more so since by using a heat exchanger heating or cooling of the solvent is not required, thus limiting the heat requirements of the process.

Removal of Water and Particulate Matter

It is obviously desirable to remove water and particulate matter from marketed products, and it is often just as important to do so as to ensure the basic performance characteristics. For example, water and particulate matter in the fuel can have disastrous effects on gas turbine blades; free water may cause corrosion throughout a fuel distribution system, and particulate matter may block filters or the fine orifices of fuel injection and burner systems.

Water may be removed physically, chemically, or electrostatically. Particulate matter may be removed by water washing, or, more generally, by filtration. Various processes used for these purposes are listed in Table XXXVI.

TABLE XXXVI
Removal of Water and Particulate Matter

Salt dryers
Electrostatic coalescing
Sand coagulators and filters
Vacuum flashing
Trace acidity control
Good housekeeping

Salt dryers

Salt dryers are used to remove water from primary distillation products, and to control the water content of materials both before and after secondary processing. The product is passed upwards through a vertical drum filled with suitably graded rock salt. Rock salt is not a powerful desiccant; it will remove the free water but only a little of the dissolved water. If more of the dissolved water has to be removed it is usual to use calcium chloride in the dryer.

Electrostatic coalescers

The Howe-Baker Superdryer (Fig. 27) uses electrical coalescing for the removal of free water, and sodium chloride or calcium chloride for the removal of any residual traces of water.

The dryer is simple to install and requires no interconnection of piping; there are no moving parts, and maintenance costs are exceptionally small. The life of the desiccant is normally two to three years.

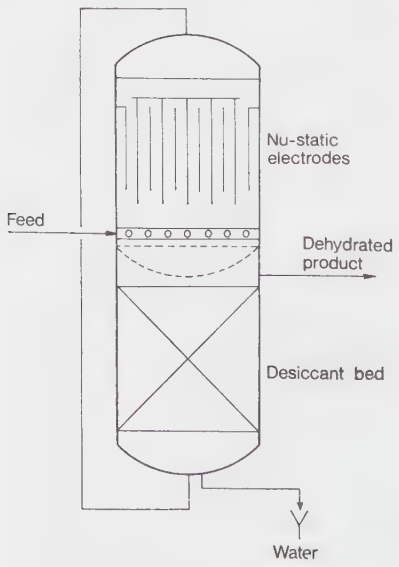


Fig. 27. Howe–Baker superdryer.

TABLE XXXVII
Howe-Baker Super Dryer: Operating Data

Charge stock	Gas oil
Charge rate, bsd	10 000
Gravity, API, 60°F	36.0
Temperature, °C	38
Inlet product, free water, ppm wt	954
Inlet product, soluble water, ppm wt	116
Inlet product, total water, ppm wt	1 070
Dehydrated product, total water, ppm wt	87
Haze point of dehydrated product, °C	19
Salt required per day, lb	36
Normal power consumption, kW	1.0

The product to be dried enters the dryer through a distribution header and passes upflow through NU-static electrodes, where free water is removed by electrical coalescing. The product then enters the desiccant bed which removes trace water. The process operates over a fairly broad temperature range, normally around 40°C.

The process is used for the dehydration of heating oil, kerosine, diesel fuel, and solvents. The dehydrated product contains no free water but may contain some dissolved water. It is clear and bright, and a haze point depression of 8–28°C is commonly achieved. Operating data for the process are given in Table XXXVII.

Sand coagulators and filters

Vertical drums filled with fine sand are often used for the physical removal of particulate matter and water, and have the advantage over salt dryers in not involving the use of chemicals. Downflow through the bed and upflow through a water separator will remove gross water, but not haze. For this purpose the oil must pass upward through the bed with a bottom water drain, so that it can emerge clear and bright from the top of the drum. A 5-micron filter may be needed for turbo-jet fuel.

Vacuum flashing

Where difficulties might be met in the removal of water from high-boiling or viscous products by the previously described methods, water may be removed by passing the product through a vessel at a sufficiently reduced pressure to cause the water to evaporate. Such a process is generally referred to as vacuum flashing, and is sometimes used for the clarification of lubricating oils.

Trace acidity control

Traces of acidity, too low to be registered by normal standard methods of test, sometimes occur in the product owing to inadequate water washing after treatments in which acids are either used or formed as intermediates during the process. This results in a particularly troublesome kind of corrosion product,

which appears to be colloidal ferric hydroxide of only about one micron particle size. Such particulate matter usually passes through all filters and, in the case of turbo-jet fuel, has been known to cause failure in the IATA aircraft refuelling millipore test.

The main problem with this kind of corrosion is that it is inherent in the product, and hence no matter how many times the product is filtered to a clear and bright condition, corrosive action continues whenever water is present. With critical products therefore, it is advisable to introduce a processing control test to ensure that the aqueous extract of the product has a pH value not less than 6 to avoid this particular kind of corrosiveness.

Good housekeeping

With increasing demand for clear and bright products, especially for critical service such as in turbo-jet and gas-turbine engines, there has been a greater realization that well-refined products may be contaminated in storage owing to the accumulation of water and corrosion products at the bottom of the storage tank. Even when a clear and bright product is pumped into a clean tank, the oil absorbs water from the atmosphere, and this water subsequently separates out on the sides of the tank and collects as water bottoms.

In consequence, and so long as oxygen is present, corrosion occurs, even when the pH of the water bottoms is quite high. In fact, so long as oxygen is present, corrosion will occur in the water bottoms regardless of the pH values.

Bacterial slime accumulates at the interface between water and oil, and ferric hydroxide forms in the water bottoms. The agitation in the tank during pumping operations disperses the water and particulate matter throughout the oil, causing a haze that is extremely difficult to remove. Such hazes are rarely due to water coming out of solution as the contents of the tank cool. Provided that the tank is clean and free from water bottoms and particulate matter a large oil-storage tank will cool through a considerable temperature interval without the oil becoming hazy. This seems to be because the rust nuclei cause the water to separate on the walls of the tank whence it trickles to accumulate at the bottom.

Good housekeeping, with regular removal of water bottoms from oil-storage tanks, pays big dividends in maintaining clear and bright products.

Molecular Sieves

The advent of molecular sieves has made it possible to achieve dewpoints below 70°C in the drying of gases, and residual water contents of 1 to 10 ppm for liquid streams.

Molecular sieves are agglomerates of crystalline sodium and calcium alumino-silicates that have been heated to remove their water of hydration. Produced from either natural or synthetic zeolites, their pore size can be controlled accurately within a small range of molecular dimensions. They facilitate the separation of gaseous or liquid mixtures by two mechanisms: absorption, whereby they have a strong preference for polar components such as water, hydrogen sulphide, and carbon dioxide; and separation by size, whereby only those molecules are retained which fit into the port openings of

the sieve. For example, a molecular sieve with an average pore diameter of 4 Å will absorb ethane but pass propane.

Separation by molecular sieves is frequently based on a cyclic operation. The gas or liquid is passed through a bed of molecular sieve, usually at ambient temperature, and high partial pressure. After the adsorbent has been saturated to a point just below where the contaminant would break through, the adsorbent is taken off stream and regenerated by heating and purging with a carrier gas, normally nitrogen or fuel gas. At the completion of the regeneration period, the adsorbent bed is cooled and returned to the process.

Sieves with 3 Å, 4 Å, 5 Å, and 10 Å pore sizes are made, each of which can be supplied as balls of 4 to 8, 8 to 12, or 20 to 50 mesh size (Tyler screening).

The 3 Å sieve is used for special drying applications in which it is essential that all molecules other than water are rejected.

The 4 Å sieve is used for general drying purposes. It replaces other desiccants when low dewpoints or high-temperature operations are required. A water adsorption capacity of 12 to 15 per cent weight is generally realized, the lower capacity at operating temperatures above 65 °C.

The 5 Å sieve is used in normal and isomer separations for the biodegradable detergents industry.

The 10 Å sieve is used mainly in catalytic and purification applications. It is steam and heat stable, an important consideration in these applications, since many adsorbed compounds are difficult to desorb.

Of the three mesh sizes, the 20 to 50 mesh is used in liquid-phase hydrocarbon separation processes where diffusion is very important to system kinetics. The small bead has a rapid rate of adsorption. With larger beads the slower rate of adsorption would result in a long mass transfer zone (no sharp break-through) so that there would be either a low useful capacity or such a slow linear velocity through the bed that throughput per day would be extremely low. Therefore, for most liquid-phase processes the 20–50 mesh bead is preferred. The 4 to 8 and the 8 to 12 mesh beads are both used for vapour, and liquid-phase processes, the 8 to 12 mesh having a faster rate of adsorption, and a higher bed pressure drop.

The important properties of molecular sieves are: attrition resistance, rapid rate of adsorption, high useful capacity, low adsorption of impurities, high stability and long life. In most high-pressure applications attrition occurs owing to pressure changes during desorption. In general the hydrocarbon separations molecular sieves exhibit a fast rate of adsorption, giving high capacity at fast feed rates and a high useful capacity. The manufacturing process provides the minimum surface for adsorption of impurities. This is important because adsorbed impurities will contaminate the adsorbent during the desorption step and reduce the product quality, and certain impurities (aromatics and olefins) tend to crack and coke the sieve surface, requiring frequent burn-off.

Molecular sieves were introduced commercially in 1954. Because of their outstanding affinity for water their first applications were for the drying of gaseous and liquid streams. They were used for drying natural gas, refinery gases, chemical process gases, and feeds to low-temperature liquefaction. In the liquid phase, they are used for the drying of kerosine, olefins, transformer oil, mixed xylenes, fluorocarbon refrigerants, benzene, and solvents.

The scope of molecular sieves goes well beyond drying, into such fields as super-drying, purification, hydrocarbon separations, and catalytic processes.

Super-drying processes

Lean absorber oil can be dried by the use of molecular sieves. This is useful in the conversion of existing ambient temperature oil absorption plants into more efficient recovery plants operated at low temperatures.

Molecular sieve drying of the feedstock offers significant improvement in both corrosion and acid consumption in alkylation by either hydrogen fluoride or sulphuric acid.

3 Å sieves are used for drying refrigerants, olefins, and methyl and ethyl alcohols.

Purification processes

Sour natural gas with a high carbon dioxide content can be purified by molecular sieve adsorption. Alkaline absorption is often uneconomic, and 5 Å molecular sieves offer the advantage of selectiveness for hydrogen sulphide over carbon dioxide.

Light hydrocarbon streams have been sweetened by liquid-phase adsorption by molecular sieves, the sulphur compounds being more polar than the hydrocarbons and therefore adsorbed.

Molecular sieves have been in use for several years to sweeten LPG. Although the method has not yet become commercial for treating higher fractions reports indicate good desulphurization and sweetening of de-ethanized natural gasoline. Since this type of sweetening involves removal of the sulphur compounds rather than mere conversion into a more desirable form, molecular sieve treatment improves the lead susceptibility of the gasoline.

Separation of hydrocarbons

5 Å molecular sieves are used to separate normal paraffins from other hydrocarbons in such processes as the upgrading of catalytic cracking stocks, purification of aromatic hydrocarbons, recovery of n-paraffins as petroleum waxes or as feedstocks for biologically soft detergents, and upgrading of jet fuels.

In isomerization, reforming or alkylation, 5 Å molecular sieves may be used instead of fractionation to separate unconverted n-paraffins from the reactor product. The components of lowest octane number are removed and may be recycled to the reactor for conversion into isoparaffins.

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II REFINING OF LUBRICATING OILS AND WAXES

Before describing the various lube finishing processes, brief mention will be made of the methods used for the manufacture of lubricating oils, since it is for this purpose that the processes are largely applied, and the techniques are rather different from those of the finishing processes considered so far.

The first step in lubricating oil manufacture is to remove the crude distillates from long residues, leaving behind in the resulting short residue, the bulk of the unwanted heavy asphaltic materials. This operation may be accomplished by vacuum distillation. Solvent extraction with propane is also used for the same purpose, and is indeed the only way of removing the heavier fractions from a paraffinic crude without an undesirable amount of thermal decomposition.

In general, the preparation of finished lubricating oils from these crude distillates involves the partial or complete removal of wax, aromatics, chemically unstable compounds, dark constituents, and acidic components. The treated lubricating oil should then be of good colour and colour stability, and have a low pour point, cloud point, ash content, and acid value. The more highly refined oils should also have a high viscosity index and oxidation stability. It is not always necessary to remove all the constituents mentioned. It is more convenient and economical to suit the oil to the application.

Lubricating oils are conveniently classified as naphthenic and paraffinic oils. Oils of high viscosity index, which are generally used for the lubrication of automotive engines, can normally be made only from paraffinic-base oils which frequently have a high wax content, and therefore need dewaxing. Naphthenic crudes do not produce high viscosity index oils, but they are quite suitable for the manufacture of oils destined for the lubrication of industrial machinery and certain types of diesel engines, and, being generally of low wax content, may not require to be dewaxed. There are, of course, exceptions to such generalizations; for example, Pennsylvanian crudes, which are paraffinic, furnish lubricating oil fractions of remarkable low asphalt, aromatic, and wax content.

It is frequently necessary to remove naphthenic acids from the oil to obtain an acceptable stability and low acidity; this is unlikely to be necessary for paraffinic crudes. Naphthenic acids can conveniently be removed during the vacuum distillation stage by the injection of alkali. The neutral distillates so prepared are treated either with 98 per cent sulphuric acid and earth or with hydrogen, for use as industrial lubricating oils.

The high-temperature stability required of high-grade lubricating oils can, in general, be obtained only by solvent extraction to remove unstable constituents. Paraffinic oils need dewaxing to obtain the desired low pour point; this step usually follows solvent extraction, but occasionally there are advantages in reversing the order of these two operations. A finishing treatment with a clay or hydrogen may be desirable to remove the last traces of unstable bodies and to improve colour.

Recent Developments

In order to meet the free-world consumption of lubricants economically, it has become necessary to minimize the costs of new plants and to integrate lube-

processing steps. Propane de-asphalting, removes asphalt from vacuum pipe-still bottoms, to permit the manufacture of high-viscosity lubes; phenol extraction, removes unstable low-viscosity-index materials; hydrofining, improves colour; and propane dewaxing reduces pour point of oils to as low as 0°F; all have been integrated by Esso in a single complex.

R. Hournac has reported[1] that there is an increasing replacement of single-grade by multi-grade engine oils to improve fuel economy, which has resulted in distillate rather than bright stock in the base oils, in order to compensate for the thickening tendency of viscosity index improvers. Problems have been caused by the resulting volatility increase in base oils. The need has grown for maximum solvent refining and hydrofinishing of bright stock to reduce Conradson carbon values. Problems have been caused by excessive hydro-treating severity due to loss of natural anti-oxidants, and of solvent power for additives, particularly with paraffinic stocks. Pollution problems demand additives compatible with emission control catalysts. Variation in the qualities of crude oils affects lubricating oil quality and yields. New concepts in old processing techniques, including vacuum distillation, de-asphalting, solvent extraction, dewaxing, incremental dilution, together with new methods of hydrocracking, and catalytic dewaxing, have helped to solve these problems.

Recent developments of lubricating oil dewaxing cover oils generally treated by solvent dewaxing; the solvents used, their properties and dilution ratios; the effects of cooling temperature and rate. Typical flow schemes and equipment for methyl and ethyl ketone and propane dewaxing methods, are now described, with reports on various other lubricant dewaxing processes, including platinum-catalysed hydrogenation.

Wax hydrofining, and catalytic hydrogenation have been developed for improving the colour, purity, and stability of wax products. These processes are applicable to a wide range of products including petrolatum, slack, paraffin, and intermediate and micro-crystalline waxes. Wax hydrofining replaces the clay or bauxite contacting processes commonly used for refining wax products which must meet colour and purity specifications.

Refining Processes

Acid/clay treatments

The older processes of treatment of lubricating oils by concentrated sulphuric acid and/or by clay, have largely been superseded by treatment with hydrogen under conditions essentially the same as for hydrofining. These old methods were described in the Fourth Edition of this book and are now considered to be obsolete.

Solvent extraction process

If an undesirable constituent is present in appreciable concentration then it is usually cheaper to remove it rather than to convert it into some innocuous form. If the constituent differs in chemical type from the main body of the material processed, then extraction with a suitable solvent will frequently be the favoured method of removal. On settling after extraction two phases are formed. The extract phase contains the dissolved components, while the raffinate phase consists of the refined oil. The solvent is recovered from the

extract phase by distillation and used again. Frequently it will also be necessary to process the raffinate for the recovery of a small amount of entrained and dissolved solvent. Sometimes solvent extraction is used to recover some valuable component rather than to remove undesired constituents.

Solvent ratios are usually rather high, sometimes reaching 10 volumes of solvent recycled per volume of feed, although ratios of the order of 2:1 are more common. Hence considerable reductions in operating cost can be effected by careful design. Extraction is usually carried out in a number of counter-current washing stages, and where the solvent is recovered by flashing it is frequently economic to use multiple effect evaporators.

While the main process variable is the solvent ratio, the operating temperature is also of significance. Usually on raising the temperature the solvent power is increased but the selectivity is decreased, resulting in deeper extraction but a lower yield of raffinate. This phenomenon may be applied for the improvement of selectivity by operating the counter-current extraction train with a lower temperature where the feed enters as compared with the point of exit of the raffinate. A subsidiary advantage of this technique, also leading to better selectivity, is the generation of what may be likened to an internal reflux, since upon entry to the warmer end of the train the solvent will dissolve appreciable amounts of 'raffinate' components; by the time the solvent leaves the train at the colder end such components will have been transferred back to the raffinate phase. On raising the temperature a point is frequently reached where feed and solvent become completely miscible and, of course, operations must be designed to take place below this temperature.

Another method of improving selectivity, giving a purer extract, is by recycling part of the extract or extract-rich phase; sometimes raffinate is recycled for a similar reason.

Many analogies may be drawn between the unit processes of distillation and solvent extraction, and this is well exemplified by noting that, just as in a distillation process the improvement in separation obtained by raising the reflux ratio has to be paid for by increased reboiling heat requirements, so also the improved separation obtained in an extraction process, either by deliberately recycling a portion of the extract or raffinate, or by setting conditions to engender the internal recycle of these phases, will increase the operating costs by requiring the use of higher solvent ratios, leading to higher thermal requirements for solvent recovery.

It is desirable that the solvent property referred to as 'light-heavy selectivity' should be satisfactory. This is usually equivalent to saying that the absorptive power (distribution coefficient) should not be markedly dependent on the molecular weight of the component extracted. If this is not so then it will usually be impossible to process a feedstock of wide boiling range. To make this clear, consider a case where absorptive power, as measured by distribution coefficient, increases as the molecular weight decreases. In order to obtain good extraction of the high molecular weight extract molecules of a wide boiling range feedstock, conditions will have to be so severe that appreciable amounts of the lower molecular weight molecules normally remaining in the raffinate phase will also be extracted. Therefore, if the solvent is highly selective in respect of molecular weight, only fractions of narrow boiling range can be satisfactorily processed.

When choosing a solvent for a particular application, the following solvent properties and operating problems should be reviewed:

(a) Absorptive power.
(b) Selectivity, both as regards component type and the 'light-heavy phenomenon'.
(c) Availability, cost, ease of handling, and toxicity.
(d) Chemical stability under both normal operating conditions and abnormal conditions, such as accidental ingress of air or water to the plant.
(e) Ease of gravity separation between solvent or extract phase on the one hand and raffinate phase or feed on the other. Tendency towards emulsion formation.
(f) Recovery of solvent.

The simplest equipment for the operation consists of a series of mixing devices each followed by a phase separator, the flows of feedstock and solvent being counter-current to one another. If short contact times are acceptable, then the mixer may be a throttled globe valve, the compact arrangement of labyrinths commercially available in the well-known Durion mixer, or even a centrifugal pump. Somewhat longer contact times are obtained by the use of a series of perforated plates mounted above one another in a vertical section of large-diameter pipe or the dog-leg type of mixer consisting of a long length of pipe wound back and forth concertina fashion. For prolonged and efficient contacting, use is made of vessels equipped with paddles, propellers, or turbine blades.

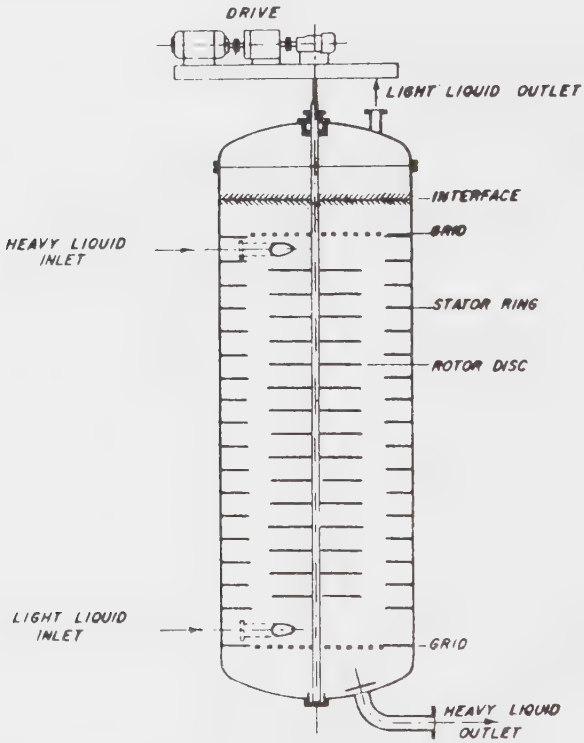
Usually the efficiency of mixing is high, the number of theoretical contacting stages achieved being close to the number installed. This is in contrast with the behaviour of certain other types of contacting equipment, such as packed towers, where the efficiency may be low and not easily predicted. Thus, mixer-settler systems are frequently used when only a few contact stages are required, but above three or four stages the equipment needed becomes too bulky. They are also adaptable to processes where emulsions are likely to form; this tendency may be readily detected and equipment changes favouring its reduction, such as decreasing the intensity of mixing, can often be made without too much difficulty.

The operating range of packed towers is frequently limited, poor contacting occurring at low throughputs and flooding at high throughputs. Especially with columns of large diameter it is difficult to obtain really even distribution of the flow of the two phases, even though redistribution devices are installed, and hence the height equivalent to a theoretical contact stage is frequently as great as 25 ft. Small amounts of suspended matter entering with the feed or formed by some corrosion mechanism in the plant will rapidly reduce efficiency. Packed towers are nevertheless widely employed for lubricating oil extraction.

Columns fitted with various kinds of perforated plates, bubble caps, and channel trays, similar to those used for distillation operations, are often favoured. They are more efficient than packed columns, but again the operating range is usually rather narrow. Their design is difficult, since proper flow of the two phases depends on an accurate knowledge of the difference in

densities. For the uncontaminated phase this is accurately known; the uncertainty rests in the extent of contamination of one phase by the other, particularly if emulsions tend to form.

Another type of contacting device which is being quite extensively installed in new solvent extraction plants is the Shell rotating disc contactor, a diagram of which is shown in Fig. 28. It consists of a vertical vessel fitted with a series of stator rings fixed to the wall, together with a central rotating shaft carrying a number of discs, one to each of the compartments formed by the stator rings.



Courtesy Hydrocarbon Processing–Petroleum Refiner

FIG. 28. Shell rotating disc contactor.

Solvent, if the heavier phase, as is usually the case, is introduced tangentially near the top of the equipment while the feed enters near the bottom. The shearing action of the rotating discs breaks up the dispersed phase into droplets which flow counter-currently to the continuous phase.

The Shell rotating disc contactor possesses several advantages over other equipment. It is compact and normally costs less to build. Operation is straightforward and flexible, a wide range of operating capacities being readily and efficiently covered. The intensity of mixing may easily be controlled by adjustment of the rotor speed.

Multi-stage centrifugal equipment designed for solvent extraction is also

available from manufacturers such as Podbielniak, Sharples, de Laval, and Westfalia Separator AG, and is in use in a number of American refineries.

Centrifugal extractors are efficient, but the equipment is usually rather costly and its maintenance somewhat specialized. No deposits must be allowed to form in the centrifuges or damaging vibrations will be set up.

Propane de-asphalting and decarbonizing

Asphalt must be removed from feedstocks destined for lubricating oil manufacture in order to avoid emission difficulties in the solvent treating step, unless the rather cumbersome and expensive Duosol process is selected for the finishing operation.

Lubricating oil fractions, except for the heaviest grades, are obtained asphalt-free by vacuum distillation. Avoidance of thermal decomposition and consideration of economic distillation operation finally control the heaviest distillate that can be obtained. The application of propane de-asphalting to the vacuum distillation residue is a convenient method of overcoming the difficulty.

Liquid propane is a good solvent for paraffinic hydrocarbons, but the bituminous constituents, with which should be included the heavier aromatics, are not dissolved appreciably. Therefore, propane is an attractive solvent for the extraction of bright stock lubricating oil components from a residual stock. Butane is less suitable, being too good a solvent for the asphaltic components, while for ethane solubilities are generally lower, leading to higher solvent ratios, and also undesirably high pressures are needed in order to maintain the ethane in the liquid phase. With propane extraction temperatures lie in the range 40 to 80 °C and pressures 400 to 550 psig. Solvent ratios are rather high, being usually between 5 and 13 to 1 by volume. Propane de-asphalting is also competitive with vacuum flashing as a means of preparing the feedstock for a catalytic cracker, and several such plants are in operation.

The flow sheet of a typical plant for propane de-asphalting of feedstock for lubricating oil manufacture is shown in Fig. 29. Extraction with solvent takes place counter-currently in a tower equipped with contacting trays of a special design. A point of difference from most other solvent extraction processes is the installation of an internal steam heater at the feed end of the tower for the purpose of maintaining a higher temperature at the extract than at the raffinate end; in other processes the raffinate end is maintained at a higher temperature than at the extract end. The reason is that propane is close to its critical point under the conditions of operation. Raising the temperature causes the propane to become more like a gas than a liquid; the solubility of paraffin falls and the selectivity is improved, contrary to the behaviour of other solvents. Another point of difference, also attributable to operation close to the critical point, is that increasing the operating pressure increases solubility, whereas normally this variable has little effect.

Propane may also be used as a dewaxing solvent, as will be described later; if the lubricating oil is to be dewaxed by the propane process, then the propane de-asphalting operation may be neatly integrated with this step by not evaporating the propane from the extract but carrying straight on to the dewaxing stage.

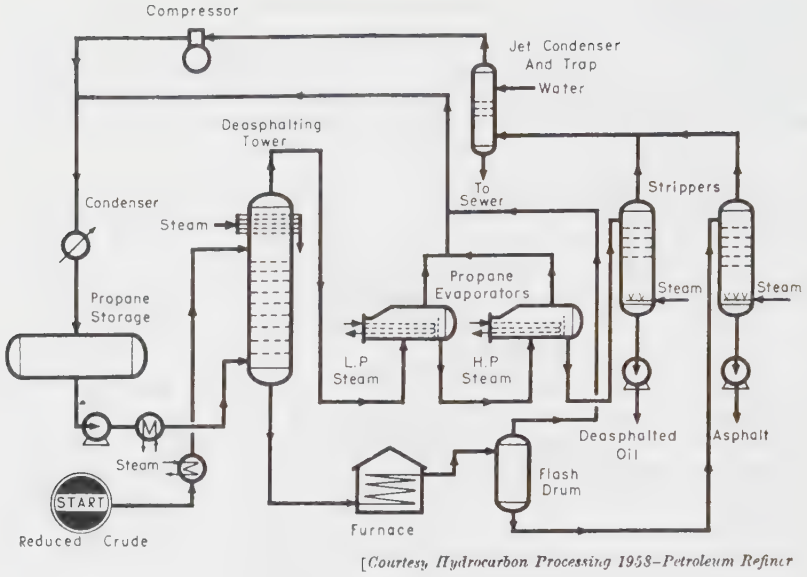


FIG. 29. Propane de-asphalting.

De-aromatization

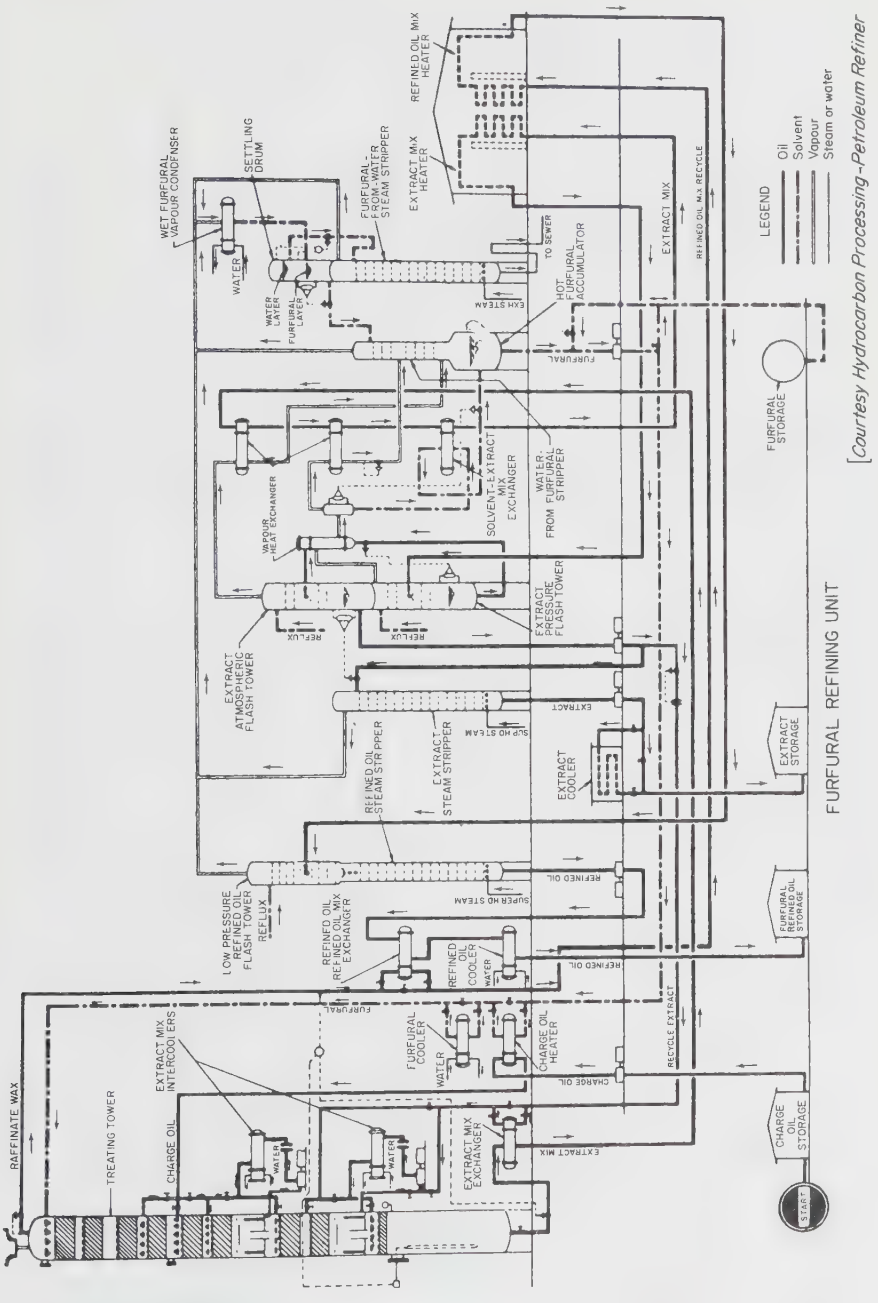
Furfural extraction

Furfural is a good selective solvent for aromatics and resins and is used extensively to improve the viscosity index and oxidation characteristics of distillate and de-asphalted lubricating oils; asphaltenes interfere with furfural extraction and their presence promotes the formation of emulsions. Kerosines, diesel oils, distillate fuel oils, and catalytic cracker charge stocks may also be processed for the removal of aromatics and contaminants with a high aromatic content, such as higher molecular weight sulphur and nitrogen compounds and resinous materials.

Furfural boils at 162°C under atmospheric pressure and is thus readily separated from the heavier lubricating-oil fractions. With water an azeotrope boiling at 98°C is formed and thus azeotropic distillation is a convenient method for the removal of furfural from lighter feedstock.

Extraction temperatures lie in the range 30 to 130°C and solvent ratios can be kept quite low, normally to between 1.5 and 3.5. Furfural is unstable at higher temperatures and, therefore, in order to prevent the formation of carbonaceous deposits and acidic components the furfural should not be heated above 232°C in the solvent recovery section of the plant. To the same end it is necessary to exclude air from the process.

A flow sheet for a typical plant for processing lubricating oil is given in Fig. 30. Points to note are the recycling of an extract phase to the packed extraction tower and the maintenance of a temperature gradient over the tower, both features being designed to improve selectivity. Flashing and steam-stripping are applied for the recovery of furfural from raffinate and extract.



[Courtesy Hydrocarbon Processing–Petroleum Refiner

FIG. 30. Furfural extraction process.

followed by azeotropic distillation to dry the furfural for re-use. A reduction in capital cost and improvement in flexibility may be achieved by replacing the packed extraction tower by a Shell rotating disc contactor.

Phenol extraction

Phenol is quite a popular solvent-refining agent in the manufacture of lubricating oils. Its use is limited to the refining of distillates, unless prior de-asphalting is practised, and in this respect it is similar to furfural. Compared with furfural, phenol has the advantage of better thermal stability, but phase separation may be more difficult. Treating is usually carried out in a tower containing plates, and an interesting feature of the process is the use of water as an 'anti-solvent'. The water, which actually contains some phenols and is available as a plant stream, is injected into the lower part of the tower, where its action is to throw out the valuable raffinate phase from solution in the solvent; thus the action is very similar to back-washing with extract or the maintenance of a temperature differential across the column for the purpose of generating an internal reflux at the base of the column. The process is described more fully later as part of the Phenolfiner section of the Esso Integrated Plant.

Exol N Process[2,3]

Exol N extraction is Exxon's selective solvent lube extraction process using *N*-methyl-2-pyrrolidone (NMP) as solvent to remove aromatics and other undesirable compounds from lube feedstocks. Cross-flow cascade weir trays have been developed, which have been successfully scaled up to extraction towers as large as 25 ft in diameter. Various solvent recovery configurations have been adapted for use with NMP. As in most modern solvent extraction processes, the contacting step in Exol N extraction is conducted in a multi-stage counter-current tower.

In the extraction tower (Fig. 31), high-boiling fractions of crude oil are

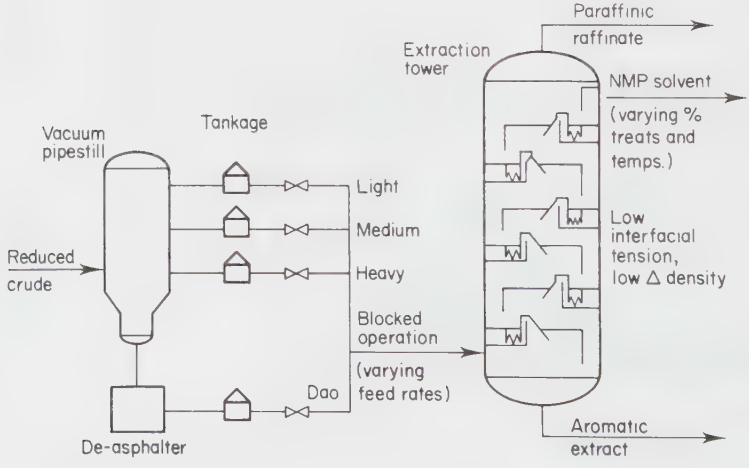


Fig. 31. NMP extraction process. (Courtesy of Exxon Research, NJ.)

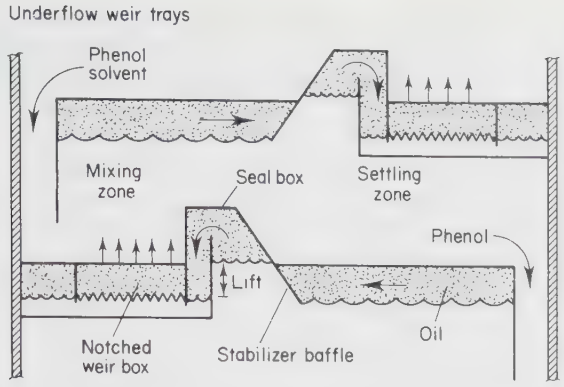


FIG. 32. Underflow weir trays. (Courtesy of Exxon Research, NJ.)

contacted with NMP solvent. This treatment selectively extracts aromatic components from the feeds to produce raffinate streams of improved quality. The trays used in the Exol N process may be of special interest because they are unlike most designs discussed in the literature (Fig. 32).

Data shown in Table XXXVIII give a dramatic example of the performance differences between an unstable underflow weir tray design with phenol solvent and an operating cascade weir tray design with NMP. The feed in both cases was de-asphalted oil from Middle East crude. The increase in bright stock raffinate yield from 45 to 82 per cent (at constant VI) resulted from several factors: the better tray design, the inherently better selectivity of NMP versus phenol, and optimized operating conditions.

Performance of NMP on a gas stripping solvent recovery scheme

This particular plant uses a simplified solvent recovery system employing gas instead of steam for product stripping—a scheme is shown in Fig. 33. Extract and raffinate solutions pass through preheat exchangers and furnaces into the flash zones of their respective recovery towers, which operate under pressure. Stripping gas is sent to the bottom of each tower to strip out remaining solvent that is not vaporized in the furnaces.

TABLE XXXVIII

Cascade versus Weir Trays with NMP. (Courtesy of Exxon Research, NJ)

Tray type	Underflow weir	Cascade weir
Solvent	Phenol	NMP
Tower diameter, ft.	19	22
Raffinate yield, %	45	82
Solv. circ., bbl/bbl raff.	5.6	3.2
Feed rate, b/d per sq. ft.	Base	16% higher (not limiting)

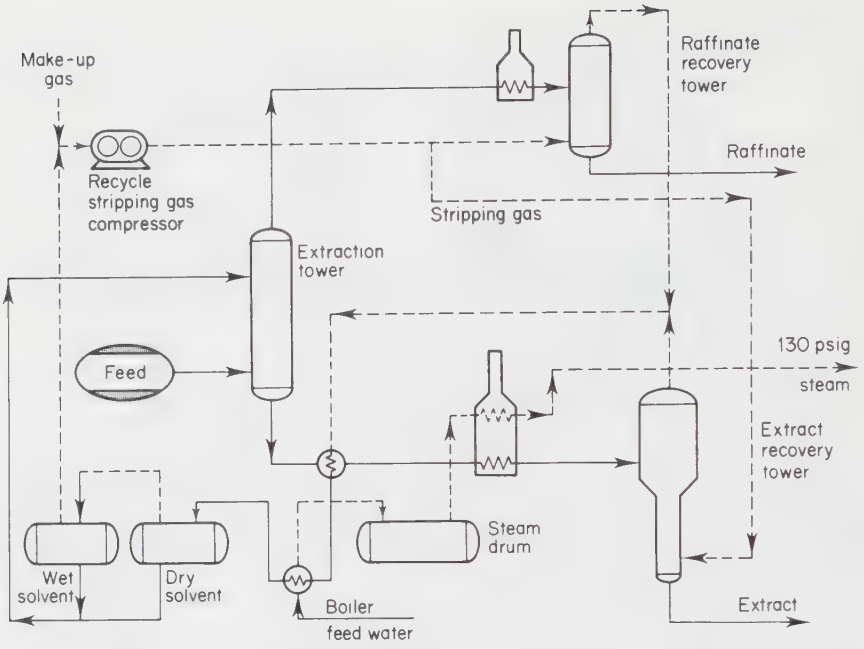


FIG. 33. Exol N extraction unit using recycled stripping gas for solvent recovery. (Courtesy of Exxon Research, NJ.)

Stripping gas and solvent vapours from the tower overheads pass through heat exchangers into the dry solvent drum, where the bulk of the condensed solvent and some water separate out.

Hot vapours from the dry solvent drum are further cooled, and wet solvent condenses out in a second drum. Stripping gas from this wet solvent drum is then picked up by a compressor and recycled. With this system, no water enters the unit, except a very small amount dissolved in the oil feed. Disposal of excess waste water containing traces of solvent is minimized. Because solvent vapour is always under pressure, most of it condenses at a relatively high temperature. All of the heat in condensing solvent cannot be used effectively for furnace preheat. The extra heat is used to generate medium pressure steam (in the range of 125 to 175 psig) or to vaporize lower boiling point solvents in an integrated de-asphalting or dewaxing unit. The system is very stable, and the net heat exported represents a large proportion of the heat input in the furnaces.

Other solvent extraction processes

The solvent extraction process used for the manufacture of lubricating oils is nearly always one of those already described. However, some plants are still using other and older processes, and brief mention will therefore be made of these. Both nitrobenzene and chlorex (dichloroethyl ether) have been used as extraction solvents, but are not much favoured nowadays.

The Duosol process is worthy of note as being a method of solvent-treating a residual oil of high asphalt content. Two solvents are used: propane, in which the desired raffinate dissolves, and Selecto, a blend of phenol and cresols, which preferentially dissolves asphaltenes, resins, unsaturates, aromatics, and colour bodies. The basic theory behind the process is that the solvent power is at its optimum when the molecular weights of the solvent and the material to be extracted are close together. Thus, if the process were to be operated with only the one solvent, Selecto, the lower molecular weight aromatics would be satisfactorily extracted but not the asphaltenes, which are high molecular weight aromatic bodies; to a considerable extent these would remain in the treated raffinate phase. However, by adding propane to the raffinate phase its molecular weight is decreased and also, therefore, its solubility for asphaltenes, which are then efficiently extracted by the Selecto.

However, there are several disadvantages of the process. The use of two solvents makes for a complicated plant by no means easy to operate, particularly since emulsion formation is quite frequently encountered. The solvent ratios are high and hence operation is costly. The great merit of the process lay in its ability to handle residual stocks, but with the advent of the propane de-asphalting process such stocks are more easily and cheaply handled by vacuum distilling to a short residue which, after propane de-asphalting, is a suitable feed material for any of the other solvent extraction processes.

Udex Process

This process, which may be applied to lube oils, is adequately described under the section concerning the improvement of performance characteristics of distillate fuels, and a flow diagram is shown in Fig. 25.

Dewaxing[4,5,6,7,8,9]

Crude lubricating oils contain certain paraffinic materials that readily crystallize out on cooling. High molecular weight n-paraffins and certain isoparaffins and cycloparaffins behave in this way.

Clearly crystallization must be prevented within the range of temperatures to which the lubricating oil will be subjected in practice, and these materials must therefore be removed, the process of removal being termed dewaxing. Dewaxing cannot be effected by distillation, since the waxy materials boil over the whole of the lubricating oil distillation range, and therefore other processes have to be employed. The oldest of these is straightforward chilling of the oil down to the required pour point temperature, followed by removal of wax by filtration at this low temperture. However, this process is now little used, mainly because of the high labour requirements for operation of the filter presses. Also it is unsuitable for processing heavy oils, because of their very high viscosity at the temperature of filtration. In order to overcome these difficulties various solvent dewaxing processes have been evolved. The first involved the addition of a heavy naphtha or gas oil to the crude lubricating oil charge. Although filtration rates were much improved by virtue of the considerable reduction of viscosity realized at the filtration temperature, the efficiency of the process suffered on account of the appreciable solubility of wax in the diluent.

Thus, when the diluent was subsequently distilled off this wax remained behind in the lubricating oil. Also these solvents did nothing to improve the rate of filtration by causing the wax to crystallize out in a form easy to filter off. While waxes consisting mainly of straight-chain molecules separate as well-defined crystals, easy to separate, those containing a high proportion of isoparaffins tend to separate as micro-crystals which are difficult to separate. The isoparaffinic waxes are usually to be found concentrated in the higher boiling fractions. When discussing solvent extraction processes earlier, mention was made of the advantages of treating a narrow cut rather than one of wide boiling range. Not infrequently this will be found true also of solvent dewaxing. Generally the formation of pasty masses of wax crystals difficult to filter may be avoided by the use of a suitable procedure when dewaxing a feed the waxy components of which do not differ greatly from one another in molecular weight. Sometimes the dewaxing of a material of wide boiling range may be so difficult that it is advantageous in the first place to fractionate the feed into light and heavy components.

In view of the shortcomings of naphtha and gas oil as diluents, other solvent aids for dewaxing have been developed. A good dewaxing solvent should comply with the following requirements as closely as possible:

(a) Complete miscibility with oil at the dewaxing temperature.
(b) Low solubility of wax in the solvent.
(c) Waxes, whether consisting of straight- or branched-chain molecules, should be separated in a form suitable for efficient filtration.
(d) Solvent should be of low boiling point for easy recovery from lubricating oil.
(e) In order to minimize operating costs the solvent/oil ratio should be low, as should also be the sensible and latent heats (assuming the solvent is to be recovered by evaporation followed by condensation).
(f) Solvent should be cheap, non-corrosive, thermally stable, and non-toxic.

Methyl ethyl ketone (MEK)/benzene dewaxing

A mixture of two solvents is frequently a better dewaxing solvent than either of them alone, and this is the case with the extensively used methyl ethyl ketone (MEK)/benzene dewaxing process. Another advantage of the use of two solvents is that the solvent composition can, if necessary, be changed as the feedstock is changed and thus maximum efficiency may be achieved over a wide range of operating conditions. The solvent used in this process normally contains 25 to 50 per cent of MEK, 49 to 60 per cent of benzene, and 12 to 25 per cent of toluene. The MEK may be regarded as the real diluent or wax-precipitating partner of the mixture; however, its miscibility with oil at low temperatures is limited, and in order to maintain the oil solution benzene is added to the formulation.

In some plants ketones of higher molecular weight have advantageously replaced MEK: the solvent so formulated has a higher solvent power for oil while still maintaining a low solubility for wax, and this leads to appreciable reductions in refrigeration costs. Pure benzene crystallizes at 5.5 °C, and the fear that benzene might 'crystallize' out should very low temperatures be

employed was one reason for including some toluene in the mixtures. Toluene is sometimes used instead of the usual benzene/toluene mixture, with improvements in the rate of filtration, since its higher oil solvent properties permit the concentration of ketone in the solvent to be increased; frequently the cost of solvent will be reduced by the change since toluene is usually cheaper than benzene.

The flow sheet of a typical MEK/benzene plant is shown in Fig. 34. After mixing with the solvent the oil charge is heated to ensure that complete solution of wax is effected; if any wax crystal nuclei are allowed to remain in the solution the crystals subsequently formed may be difficult to filter. The mixture is then chilled to the required filtration temperature, which is usually of the order of $-20°C$, first by heat exchange with the cold filtrate and then by liquid ammonia or propane refrigerant. Pipe-in-pipe type heat exchangers are usually employed for this duty; the oil flows through the inside pipe, the surface of which is kept free of wax by a system of rotating spring-loaded scraper blades in order to maintain an efficient rate of heat transfer.

The wax is removed by filtration under vacuum in rotary filters. The wax cake collected on the filter drum is washed with chilled solvent, blown off with inert gas, and transferred by a conveyor to the wax-mix flow tank from which the mixture is then pumped to the solvent recovery system.

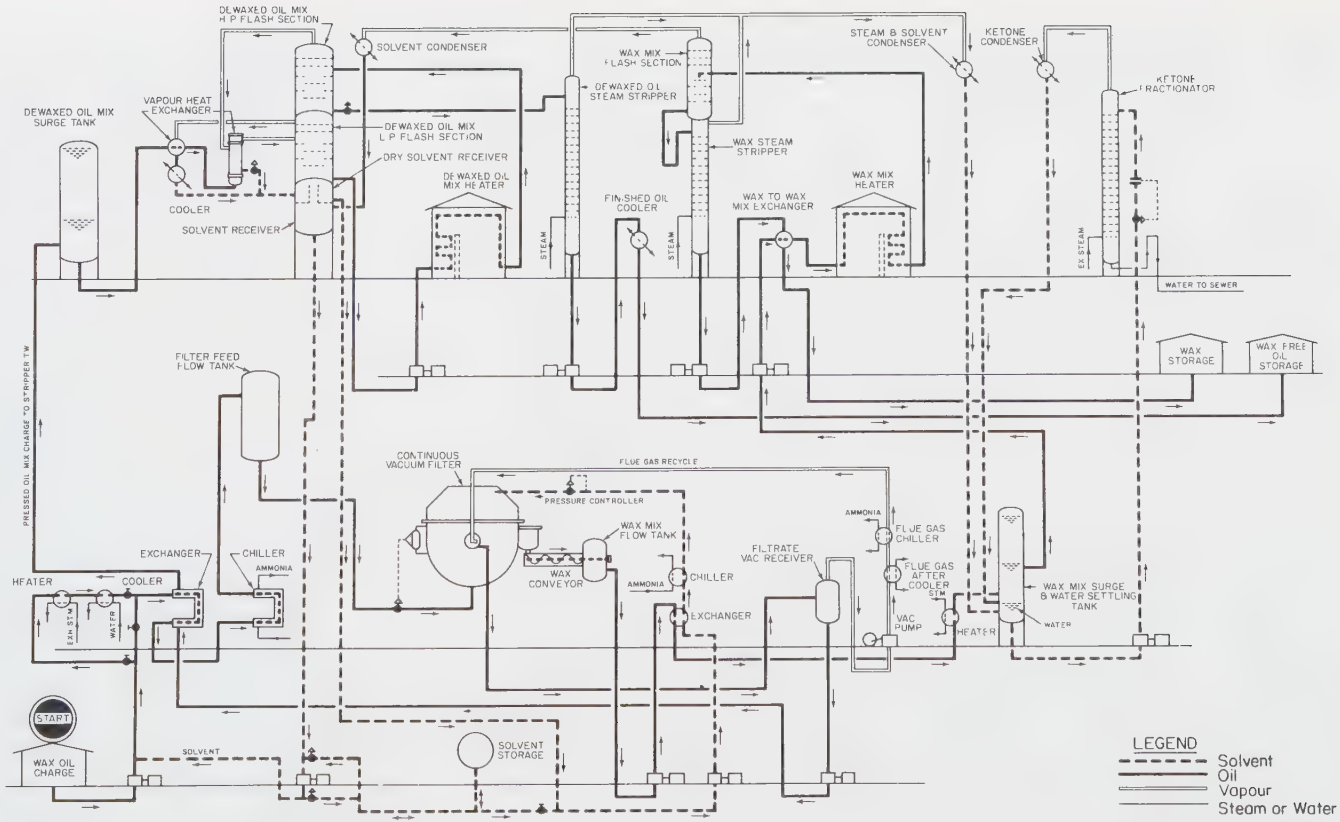
Solvent is recovered from both the dewaxed filtrate and the separated wax by evaporation. A double-effect flash-evaporation system for recovery of solvent from the filtration has been installed in the plant described here to obtain a good thermal efficiency.

Water enters the plant, since stripping steam is used in the final stages of solvent recovery; there may also be some water present in the feed. It is removed from the solvent as a bottom stream in the ketone fractionator. The overheads from this column consist of an azeotropic solvent mixture and are recycled. Solvent ratios normally lie between 1:1 and 4:1. Chilling rates of 2 to 7 °C per minute may normally be applied without obtaining crystals so small that only very low filtration rates are possible. Low pressures exist throughout the process.

Propane dewaxing

Propane is extensively used as a dewaxing solvent and is frequently competitive with the MEK/benzene process. Compared with the latter process, propane dewaxing has the advantages of requiring a solvent of only one component and of not requiring the installation of a separate refrigeration system, since chilling may be accomplished by the evaporation of part of the solvent stream. Water removal is easily achieved, since water is relatively insoluble in propane. If a residual oil is to be processed then a very neat operation may be carried out with propane, first applying propane de-asphalting and then following up with propane dewaxing without separating propane and oil in the stage intermediate between the two processes.

There are, however, certain disadvantages of the process. Propane is not a very selective solvent, and thus dewaxing temperatures must be rather low in order to compensate for the relatively high solubility of wax in propane. High-pressure equipment is required in order to maintain the propane in the liquid



[Courtesy Hydrocarbon Processing-Petroleum Refiner

FIG. 34. MEK/benzene dewaxing process.

state. Careful control of the operating conditions is necessary in order to obtain readily filterable wax crystals, and gel formation is likely to occur at solvent ratios below 1.6:1.

Frequently the presence of small quantities of asphaltic matter has a desirable effect on filtration rates. If propane dewaxing immediately follows de-asphalting, sufficient material of this type should already be present to assist filtration, but if solvent extraction is applied as an intermediate step, this may no longer be true, and it may be advantageous to add a small amount of some proprietary brand of pour point depressant such as 'Santopour' or 'Paraflow'.

A flow sheet of the process is given in Fig. 35. Here the pipe-in-pipe chillers of the MEK/benzene process have given way to direct evaporation chillers, and the solvent recovery system is relatively simple.

Dewaxing with chlorinated solvents

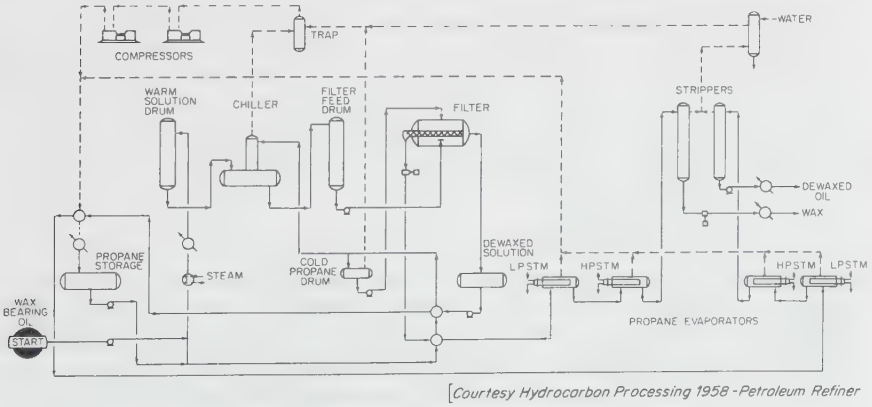
Chlorinated solvents may be used for dewaxing in a similar manner to that described under MEK/benzene dewaxing. In the Edeleanu DiMe dewaxing process using mixtures of 1,2-dichloroethane and methylene chloride, ratios are typically 70:30 to 50:50 by volume, depending on charge stock viscosity, and solvent ratios have been given as 320 volume per cent to 550 volume per cent on feed, again depending on oil grade. Filtration temperature is about 3 °C below the required dewaxed oil pour point.

The older centrifugal processes utilizing the high density of chlorinated solvents as a means of separating wax from oil/solvent mixtures do not appear to be favoured nowadays.

Chlorinated solvents tend to liberate hydrochloric acid at higher temperatures and also by the action of steam, and this behaviour must be taken into account when designing the solvent recovery systems.

Urea dewaxing

Urea and various straight-chain organic compounds are capable of forming addition complexes with waxes, called adducts, which are crystalline at room



[Courtesy Hydrocarbon Processing 1958 - Petroleum Refiner

Fig. 35. Propane dewaxing process.

temperatures. By raising the temperature and or diluting with a suitable solvent, which may even be the purified oil, it is possible to resolve the adduct into its constituents.

The mechanism is neither true adsorption nor the formation of a loosely-bound molecular complex, but bears certain similarities to both these phenomena. In the free state, urea crystallizes in a tetragonal form, but when adducts are formed the crystals are hexagonal, and it is into the 'canal' so formed that the molecules of the adduct former fit. At first sight one very attractive use for the reaction appears to be the dewaxing of lubricating oil stocks, since many of the waxy bodies, especially those of lower boiling point, are of a predominantly straight-chain nature. However, the early promise of the process does not appear to have been realized, possibly because of the presence in the feedstock of high freezing point materials not of a normal paraffinic structure, which are, therefore, not removed, and the fact that one, or more frequently two, solvents such as methanol-water or methyl chloride must be provided both to dissolve the urea and to reduce viscosity to the point where reaction and filtration rates are up to an acceptable level. Thus, the plant is complex and rather costly to operate. Also losses of urea may be quite high, since urea hydrolyses to an appreciable extent under the processing conditions.

Urea dewaxing is used commercially for the recovery of n-paraffins from gas oils and for the preparation of low pour point middle distillates. The n-paraffins are used as wax cracking feedstock and for olefin production. The continuous process developed by Edeleanu GmbH., Germany, is based on the use of highly saturated aqueous urea solutions, with methylene chloride as solvent and activator. Reaction temperatures in the range 20 to 45°C are conveniently controlled by regulating the evaporation of the methylene chloride, which boils at 40°C. The adduct is filtered by simple travelling-belt screens or pressure filters, and is then passed to a decomposition section. Urea solution, after concentration, is recycled to the reaction vessel. The n-paraffin or wax finally passes through a solvent recovery section.

Esso DILCHILL Dewaxing Process[10,11,12]

The DILCHILL dewaxing process permits improvements in the performance of the dewaxing step, and facilitates the production of low oil content slack wax, and also refined wax without the need for wax recrystallization.

Key elements in the efficiency of a dewaxing process are the dewaxed oil yield and the filtration rate. The first is a measure of how completely the oil separates from the wax, and the latter, how fast it does so. Both of these factors are strongly influenced by the type of crystal into which the wax is formed. It is desirable to have a large average crystal size, few or no fines, and dense crystals which occlude little oil.

Any given feedstock contains not one, but many different 'wax' molecule types of different melting points and structure. Actually, the terminology, 'wax crystal', is somewhat misleading. What is really meant is a crystalline agglomerate usually composed of a combination of mixed crystals and eutectics of a large number of mainly normal and isoparaffin molecules of varying molecular weights. When one considers the range of feedstocks that a typical dewaxer has to handle successfully, the difficulties are multiplied. In the ketone

process, the crystals are grown in a continuous plug-flow crystallizer, and there is no opportunity for recycle of fines to the crystallization zone for further growth, in contrast to the case in many industrial crystallizers. Although the effects of some process variables in wax crystallization are known directly from observations and fundamental considerations, commercial practice is based to a considerable extent on 'art' or 'know-how'. Consequently, scale-up of small-scale laboratory research findings to a commercial plant involves so many undefined variables that it is fraught with considerable risk.

The mechanical restrictions imposed by scraped surface exchangers can be eliminated if the cooling is done by mixing cold solvent with the feed.

The system used with the DILCHILL dewaxing process is shown in Fig. 36. Warm, waxy feed is injected into a crystallizer which has adequate hold-up time for proper chilling rates. It is provided with mechanical agitation, but has no indirect heat exchange surfaces. The entire chilling in the crystallizer is accomplished by adding cold dilution solvent in appropriate quantities depending on the feedstock. The excellent crystals formed in the crystallizer may be sent directly to the rotary filter, but usually they are cooled further in a small number of scraped surface chillers. The need for supplemental scraped surface chilling depends on the desired pour point of the dewaxed oil, and on the solvent dilution ratio and the temperature. The important thing is that in practical cases, the relatively small amount of scraped surface chilling does not destroy the unique crystals formed.

Overall chilling rate is set by the size of the crystallizer, while the agitation level is controlled by mechanical devices which are not hampered by having to function as scrapers as well. There is essentially no pressure drop across the crystallizer and no need for frequent depressuring to melt out wax which sticks to the internals of scraped surface exchangers. As a result crystallization conditions can be kept constant, and unit performance is much more consistent.

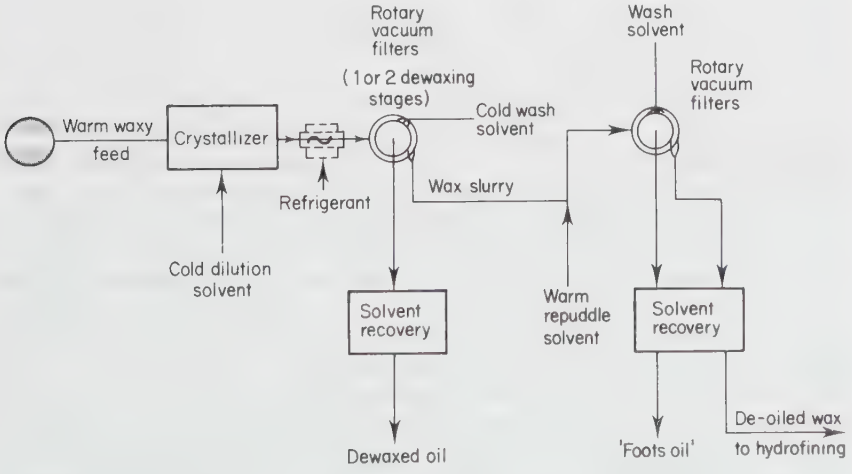


FIG. 36. DILCHILL solvent dewaxing-de-oiling process. (Courtesy of Exxon Research, NJ.)

Slack wax from the DILCHILL dewaxing process can be de-oiled without recrystallization.[10]

BP Catalytic Dewaxing Process[13,14,15,16,17]

The BP process uses a noble metal zeolite catalyst to hydrocrack selectively the paraffinic components in the feedstock. The zeolite support has the correct pore structure to be selective for normal and slightly branched paraffins. As a result, the active sites of the catalyst effectively come into contact only with paraffinic chains and enable selectivity to be maintained when processing feeds with high nitrogen and sulphur contents. For this reason little desulphurization or denitrogenation is observed. The catalyst also contains a noble metal which performs a hydrogenation function. Breakdown products from the cracking reaction are rapidly hydrogenated, thereby minimizing carbon deposition on the catalyst and leading to a highly stable catalyst system.

The consumption of hydrogen is influenced by the severity of operation required and the feedstock characteristics. Generally, consumption is in the range of 100–900 SCFB.

Process Conditions and Flow Sheet

Catalytic dewaxing is a mild hydrocracking process and, therefore, has to be operated at elevated temperatures and hydrogen partial pressures. In general, the process can be operated within the following range of conditions:

Hydrogen partial pressure (bar)	20–100
Liquid space velocity (v/v/h)	0.5–5
Catalyst temperature (C)	285–400
Gas recycle rate (Nm^3/m^3)	330–830

Within the ranges set out above, the conditions for a particular dewaxing operation will depend upon the nature of the feedstock and the required product pour point or cloud point.

A flow diagram for a typical dewaxing unit is shown in Fig. 37. Feed from storage is mixed with recycle gas and heat exchanged with reactor effluent before being heated to the required reactor inlet temperature by a fired heater. The reactor feed passes downflow through the reactor. Because the reaction is exothermic, it is sometimes necessary for cold recycle gas to be injected between the catalyst beds to limit the temperature rise. The reactor effluent is cooled against the reactor feed before passing to a hot high-pressure separator. The gas from this separator is cooled and then passed to a cold high-pressure separator. The gas from the cold separator is recycled to the reactor inlet via a gas treatment section and a recycle gas compressor.

The liquid hydrocarbons from the two high-pressure separators are combined and flow to a low-pressure separator where off-gas is removed. The remaining liquid passes to a product stripper where LPG and gasoline are removed as overheads fractions. The dewaxed oil is produced as a bottoms fraction.

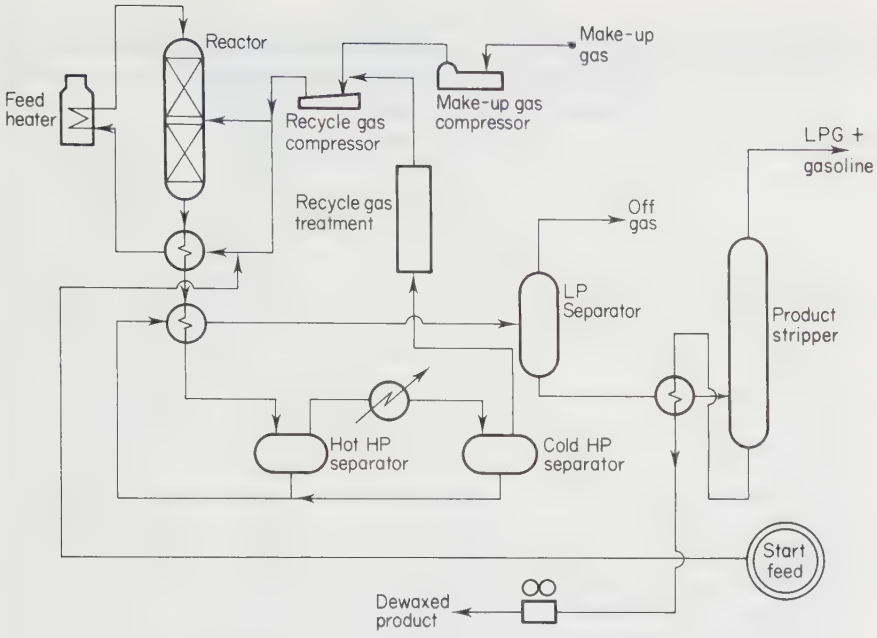


FIG. 37. Flow diagram BP catalytic dewaxing process. (Courtesy of BP Research, London.)

Applications of the BP Catalytic Dewaxing Process

Catalytic dewaxing has a wide range of applications. However, its principal use will be in two main areas:

(a) Production of speciality oils and lubricating oils.
(b) Production of low pour point middle distillates.

Production of speciality and lubricating oils. Some oil products, for example transformer oils, refrigerator oils, and certain hydraulic fluids, have a low pour point specification. Traditionally, these products have been made using low wax naphthenic crude. However, such crudes have become increasingly expensive and supply can be limited. The BP catalytic dewaxing process gives the refiner flexibility in producing these speciality oils from a wider range of paraffinic crudes.

The selectivity of the catalytic dewaxing process results in substantial improvement in cold properties of the oil, together with a small improvement in colour. A further processing step, usually solvent extraction or hydrogenation, is required to meet all quality specifications.

Table XXXIX shows the properties of transformer oil prepared by two possible processing routes from a Kuwait light vacuum gas oil. Both oils meet all of the International Electrotechnical Commission (I.E.C.) Class II

TABLE XXXIX

Production of Transformer Oil to LEC Class II Specification Using a Combination of Catalytic Dewaxing and Solvent Extraction. (Courtesy of BP Research, London)

	Solvent extraction followed by catalytic dewaxing	Catalytic dewaxing followed by solvent extraction	I.E.C. Class II specification
Density at 20°C	0.850	0.850	0.895 max
Kinematic viscosity, cSt :			
at 20°C	18.3	15.75	25 max
at −30°C	550	444	1800 max
Pour point (°C)	−45	−51	−45 max
Flash point (°C)	168	146	130 min
Neutralization number (mg KOH g)	0.01	0.01	0.03 max
Corrosive sulphur	None	None	None
Loss tangent at 90°C	3.5×10^{-4}	1.7×10^{-3}	5×10^{-3} max
Oxidation test:			
Sludge (wt %)	0.03	0.06	0.10 max
Acidity after oxidation (mg KOH g)	0.15	0.35	0.40 max

transformer oil specifications. Generally, the route in which catalytic dewaxing follows solvent extraction is preferred for the following reasons:

a) Smaller dewaxing capacity needed.
b) Reduced dewaxing severity.
c) Slightly better finished product quality.

In the preparation of refrigerator oils, catalytic dewaxing has some limitations with respect to the viscosity grades that can be produced. The higher viscosity oils tend to contain microcrystalline wax which cannot be removed by catalytic dewaxing and, therefore, the degree of pour point reduction which can be obtained is limited. However, the lower viscosity grades are particularly amenable to catalytic dewaxing, and finished oils of very high quality can be produced. Table XL shows the properties of refrigerator oil obtained from an Iranian light vacuum gas oil by solvent extraction followed by catalytic dewaxing.

The low values for floc point and Freon insolubles show that catalytic dewaxing has successfully removed all wax from the feedstock.

Catalytic dewaxing can also be used as an alternative to solvent dewaxing for the production of low pour point lube oils of medium viscosity index. For lubricating oil expansion projects, consideration can be given to the use of catalytic dewaxing for low-viscosity oils and to utilizing existing solvent dewaxing capacity for high-viscosity oils.

Production of low pour point middle distillates. Catalytic dewaxing can be used to lower the pour point of heavy gas oil fractions to make them suitable for inclusion in winter specification middle distillate blends. Table XLI gives

TABLE XL

Production of Refrigerator Oil Using Solvent Extraction and BP Catalytic Dewaxing. (Courtesy of BP Research, London)

Feed: Iranian Light Vacuum Gas Oil	
Kinematic viscosity (cSt):	
at 20°C	59.6
at 37.7°C	24.8
at 98.9°C	4.2
Pour point (°C)	−40
Flash point (°C)	196
Neutralization number (mg KOH/g)	0.01
Ash content at 775°C (wt %)	<0.01
Floc point (°C)	−51
Freon 12 insolubles at −40°C (wt %)	0.01

examples of how catalytic dewaxing can be used to reduce the pour point of heavy gas oils from three different crude sources of varying wax content. In such operations it is relatively simple to change the product pour point by adjusting the catalyst temperature. In the case of sample A, pour points as low as −36°C could be obtained. If a low sulphur content gas oil product is required, then a hydrofining step can be added either before or after catalytic dewaxing.

The main breakdown products obtained from BP Catalytic Dewaxing are saturated paraffins in the range C_3–C_8 (Table XLII).

Utility Requirements

Utility requirements for a BP catalytic dewaxing process will depend upon the particular application, and it is difficult to give more than a general

TABLE XLI

BP Catalytic Dewaxing for the Production of Low Pour Middle Distillate. (Courtesy of BP Research, London)

Crude source	A	B	C
Feed inspection:			
Pour point (°C)	+16	+27	+24
Sulphur (wt %)	1.92	1.73	0.43
Viscosity at 50°C (cSt)	7.96	12.37	—
Wax content (wt %)	11.0	16.5	20.0
Distillation (°C):			
10 wt %	332	327	286
50 wt %	381	408	349
90 wt %	411	457	424
Product inspection:			
Pour point (°C)	−20	−20	−23
Viscosity at 50°C (cSt)	9.04	16.35	

approximation of the utility requirements. For a 10 000 BPSD low pour point speciality oil application, utilities are estimated to be:

Electricity (kW)	680
Heat absorbed (Btu/hr)	12.5×10^6
Medium pressure steam (lb/hr)	8620
Cooling water (lb/hr)	165 000

Hydrofining/Hydrotreating

Hydrogen is now widely used in the refining of lubricating oils owing to the availability of abundant by-product hydrogen from naphtha reforming. Hydrogen treating processes for refining lubricating oils have been classified as hydrofining, mild hydrotreating, and severe hydrotreating. Esso's hydrofining is used to finish solvent-extracted base stocks; mild hydrotreating is used in the manufacture of a variety of lubricants and speciality products, and for the production of naphthenic oils; severe hydrotreating produces high viscosity index oils from raw petroleum feedstocks.

TABLE XLII
BP Catalytic Dewaxing for the Production of Low Pour Middle Distillate

Distribution of breakdown products (output basis): Crude source	A	B	C
Methane + ethane	0.1	0.4	0.1
Propane	2.5	5.2	3.8
Butanes	6.4	9.4	11.0
C_{5+} gasoline	8.2	10.4	16.3
Dewaxed oil	82.8	74.6	68.8

Hydrofining Process (Esso)

Hydrofining stabilizes the undesirable oil components by mild catalytic hydrogenation. Oxygen-containing compounds, for example, are converted into lower boiling hydrocarbons and water. Similarly, sulphur and nitrogen compounds react to form hydrogen sulphide and ammonia. Generally hydrofining removes virtually all the oxygen and 50 per cent or more of the sulphur, and some of the nitrogen. The conditions are usually too mild to affect hydrocarbons, although unstable bonds may be saturated.

Hydrofining is a catalytic process, and makes use of relatively simple equipment. As shown in Fig. 38, the plant consists basically of a heater, reactor, and stripping system. The feed and hydrogen are heated in a furnace before being passed together down through the reactor. The product flows into a separator where the hydrogen and its reaction products, hydrogen sulphide, ammonia, and water, and traces of light hydrocarbons are disengaged from the liquid product. Steam stripping removes dissolved gases and, finally, traces of water are eliminated in a vacuum dryer. Typical quality improvement data are given in Table XLIII.

TABLE XLIII

Hydrofining Lubricants. (Courtesy of Esso Research, Abingdon)

Crude source	Leduc		Leduc		Panhandle		Coastal		Colombian		Tia Juana	
	Feed	Product	Feed	Product	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Viscosity, SSU/100°F	607.0	587.0	1 708.0	1 670.0	326.0	302.0	1 067.0	1 018.0	1 512.0	1 068.0	2 190.0	1 470.0
Viscosity Index	87.0	87.0	89.0	89.0	101.0	102.0	65.0	66.0	12.0	27.0	32.0	45.0
Colour, Tag Robinson	7.0	21.0	1.0	11.0	4.0	16.0	3.0	12.0	2.0	11.0	1.0	9.0
Colourhold, Tag Robinson	4.0	20.0		10.0	4.0	15.0		11.0	1.0	9.0		6.0
Sulphur, wt %	0.19	0.04	0.20	0.07	0.35	0.10	0.15	0.12	0.93	0.43	1.80	0.82
Gravity, °API	28.1	28.3	26.8	26.9	29.9	30.8	24.9	25.2	20.0	21.6	19.3	21.8
Flash (COC) °F	480.0	495.0	570.0	580.0	465.0	450.0	485.0	485.0	470.0	445.0	500.0	460.0
Pour point, °F	20	25	25	30	10	35	15	20	0	15	5	10
Conradson carbon, wt %	0.04	0.02	0.27	0.16	0.03	0.02	0.08	0.07	0.22	0.08	0.88	0.33
Neutralization No.	260.0*	22.0*	1 200.0*	20.0*			0.12	Nil	2.30	0.01	0.94	Nil

* Steam emulsion no.

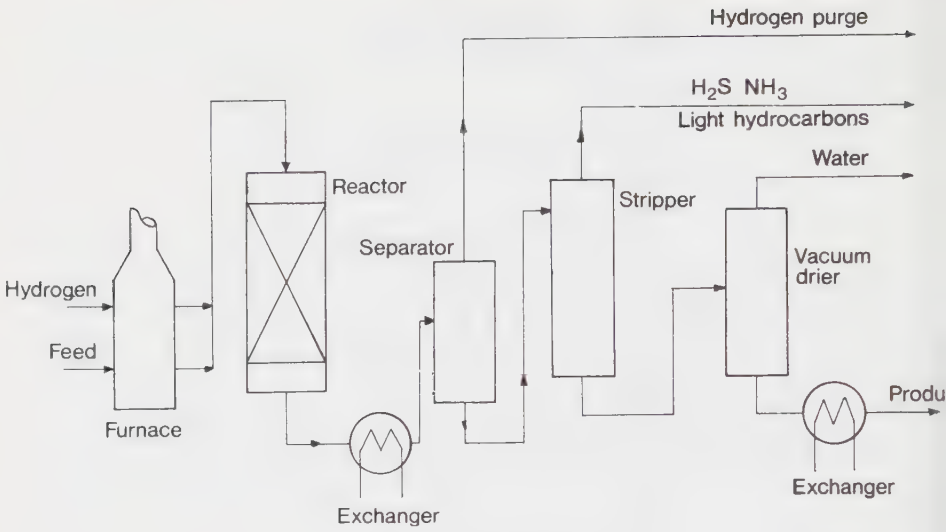


FIG. 38. Hydrofining process.

A variety of catalysts may be used; generally those consisting of oxides of elements from Group VIII and Group VIB supported on alumina have been found most effective.

Reactor temperatures range from 200 to 425 °C and pressures from 100 to 1200 psig. Space velocities can be as high as 2 v/hr/v. Considerable interchange of pressure, temperature and space velocity is possible, and usually optimum conditions can be developed, depending on the nature of the feedstock and the type of product desired.

Mild Hydrotreating Process

Naphthenic oils are widely used as process oils, and as general industrial lubricants where low cost and good colour, and colour stability are the major requirements. Nitrogen compounds appear to be largely responsible for poor colour and colour stability, and marked improvement in these respects is obtained by mild treatment with hydrogen, which achieves a significant reduction in the nitrogen compounds.

Figure 39 is a flow diagram of the process. The plant is similar to the hydrofining unit illustrated in Fig. 38, the major difference being the addition of a vacuum distillation column for topping the hydrotreated products.

TABLE XLIV

Utilities for a Typical 10 000 B/SD Hydrofining Unit. (Courtesy of Esso Research, Abingdon)

Steam	Power	Cooling water	Direct fuel
12 500#/hr	250 kW	3 100 GPM	50 mmbtu/hr

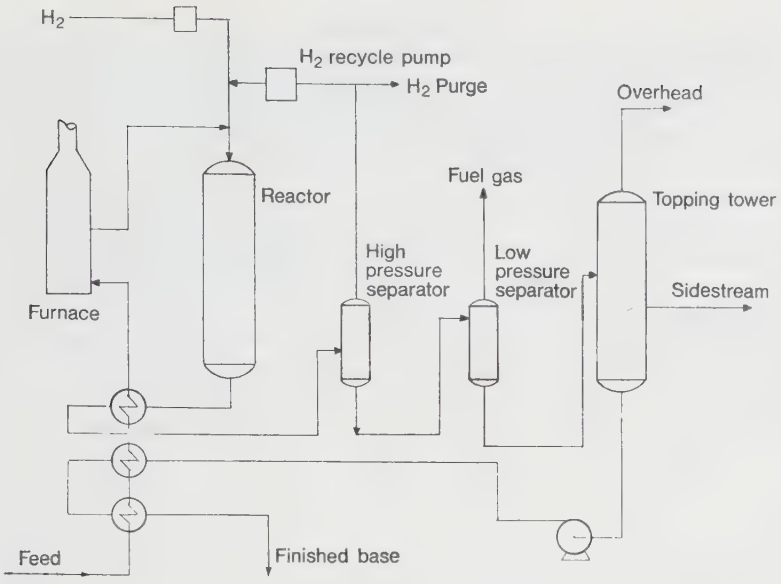


Fig. 39. Mild hydrotreating process.

The process is carried out at constant temperature and pressure; temperatures between 260 and 425 °C and pressures up to 400 psig are usually required. The space velocity of the feed is varied to produce the desired level of product quality. Catalysts of the type used in hydrofinishing are usually equally suitable for mild hydrotreating.

Economics

On-site investment and operating costs for a Hydrofiner will vary depending upon location, crude source, feed, catalyst, purpose of the treatment, and other factors.

The utility requirements for a typical 10 000 B/SD Hydrofiner are shown in Table XLIV.

BP Ferrofining Process

The BP ferrofining process was developed to produce a variety of lubricating oils finished to the specifications required for blending. The quality improvement made by ferrofining is principally on basestock colour (ASTM D1500) and this is achieved by *mild processing with hydrogen over a fixed-bed catalyst.* Compared with the alternative of using acid and clay treatment, the BP ferrofining process avoids environmental problems from the disposal of obnoxious wastes and gives higher yields of finished products.

Oil characteristics such as viscosity, viscosity index, pour point, and carbon residue are not significantly affected by the BP ferrofining process. The demulsification properties as measured by Demulsification Number IP 19 are improved and the uncatalysed oxidation stability as measured by IP 48 may also increase.

Process Conditions and Flow Sheet

Ferrofining consists essentially of passing the lubricating oil and hydrogen through a fixed bed of catalyst under mild conditions of temperature and pressure. A simplified flow diagram of the process is shown in Fig. 40.[13] The mixture of oil and hydrogen-rich gas passes through the furnace where it is raised to treatment temperature and then flows down the fixed catalyst bed in the reactor. The oil and gas leaving the reactor are separated in two stages. In once-through operation gas from both high-pressure and low-pressure stages is passed to the refinery fuel gas mains, whereas in recycle operation the high-pressure separator off-gas is returned to the reactor inlet using a recycle gas compressor. Oil from the second-stage separation is stripped with steam to obtain a product with the required flash point and then dried in a vacuum drying column. Finally, the finished oil is pumped to storage through a

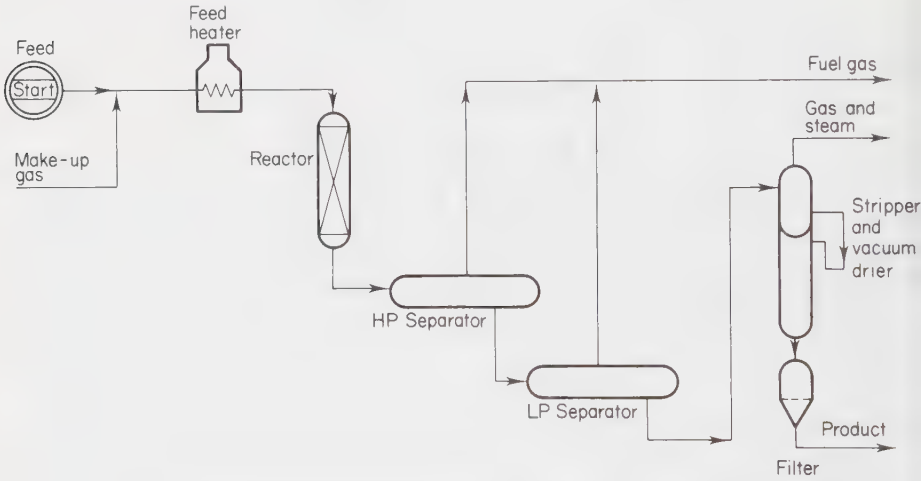


Fig. 40. Flow diagram BP ferrofining process. (Courtesy of BP Research, London).

replaceable cartridge-type filter to remove any trace amounts of solids which might have been carried forward from the plant.

The process can be designed to operate at pressures down to 20 bars, which is below the operating pressure of many catalytic reformers. Consequently, the ferrofining unit can, in suitable circumstances, be designed to operate without make-up gas or recycle hydrogen compressors, offering large savings in capital and operating costs.

Chemical hydrogen consumption is low, not exceeding 25 SCFB ($5\ Nm^3/m^3$), and for normal operations hydrogen recycle is not required. The mild operating conditions employed enable very high yields to be obtained (typically 98% wt refined stripped product).

Typical properties of ferrofined oils from Middle East crude are presented in Table XLV and an estimate of typical utilities consumption is given in Table XLVI.

TABLE XLV

Typical Properties of Ferrofined Oils from Middle Eastern Crudes. (Courtesy of BP Research, London)

Grade	Ferrofiner feed	Ferrofiner product
150 Neutral—100 VI		
Colour (ASTM D1500)	L1.5	Lo.5
Demulsification Number (IP 19)	120	60
Oxidation Stability (IP 48)		
Ramsbottom carbon increase, % wt	0.81	0.5
Viscosity ratio	1.33	1.23
500 Neutral—95 VI		
Colour (ASTM D1500)	L2.5	L1.5
Demulsification Number (IP 19)	330	180
Oxidation Stability (IP 48)		
Ramsbottom carbon increase, % wt	1.18	0.50
Viscosity ratio	1.51	1.23
150 Solvent Brightstock—95 VI		
Colour (ASTM D1500)	5.0	L4
Oxidation Stability (IP 48)		
Ramsbottom carbon increase, % wt	1.4	0.5
Viscosity ratio	1.6	1.3

Severe hydrotreating process—hydrocracking[18]

Severe hydrotreating differs from mild hydrotreating by the use of conditions which induce extensive hydrocracking in addition to saturation of aromatics and destructive hydrogenation of non-hydrocarbons. As a result of hydrocracking the process brings about substantial improvements in viscosity index, permitting oils of high viscosity index to be made without prior solvent extraction.

TABLE XLVI

BP Ferrofining Process Estimated Utilities Consumption. (Courtesy of BP Research, London)

Typical requirements, units per barrel of feed:

Electricity*	kWh	0.7
Fuel†	thousand Btu	27
	thousand kcals	6.8
MP steam‡	lb	10
	kg	4.5
LP steam§	lb	10
	kg	4.5
Cooling water (30°F rise)	US gall	215
(17°C rise)	m^3	0.81

* Includes pumps, recycle gas compressor and air coolers. Make-up gas compressor (if needed) requires an additional 0.1 kWh for each 10 atmospheres pressure increase.

† Duty to oil.

‡ 175–200 psig (12–14 bar gauge) for ejectors.

§ 24–40 psig (1.7–2.8 bar gauge) for stripping.

Hydrocracking involves scission of both saturated rings and chains. Ring scission leads to increases in viscosity index, low viscosity index components such as polycyclic aromatics being converted by a combination of hydrogenation and ring scission into compounds of higher viscosity index. In the ideal case, single-ring compounds with long alkyl side-chains are formed which may have viscosity indices of 125 or higher.

Chain scission, however, results in the formation of products which boil below the lubricating oil range, and high, as well as low viscosity index material may be lost in this way. Hydrotreating conditions which favour hydrocracking of rings in preference to chain scission are required, therefore, to produce high yields of high viscosity index oils.

The process for severe hydrotreating is similar to that for mild hydrotreating shown in Fig. 39, but the equipment must be designed to achieve greater severity. Hydrocracking is induced by operating at higher reaction temperatures and by the use of a catalyst that promotes ring scission. The hydrotreated product must again be topped to remove fuel products and light lubricating oil.

Oils from the severe process are dewaxed to meet the necessary pour point requirements. Narrow, or wide-cut streams can be processed. In the case of wide-cut feeds, the product may be fractionated by vacuum distillation, either before or after the dewaxing step.

Severe hydrotreating can produce a wide range of high viscosity index oils from low-quality feedstocks. Product yields and quality are at least as good as those obtained by solvent-extraction processes. Moreover, oils with viscosity indices of 120 to 130, which cannot normally be made by solvent extraction, are readily produced by the hydrotreating process. Base stocks of this type are advantageous for the formulation of multi-grade oils. In addition to high viscosity index base oils, hydrotreating also yields high-quality light lubricating oil, diesel fuel, and gasoline as by-products.

Hydrocracking for the manufacture of lubricating oil is described comprehensively in a paper by Gilbert and Walker[18] of Imperial Oil, from which the following résumé of the main concepts is freely taken.

Flow plan

Several lube hydrocracking processes have been described in the literature.[26,27,28,29] All involve the same basic fixed-bed catalytic system shown in Fig. 41, which is typical of hydrotreating processes in general. Oil and hydrogen are preheated and then passed downward through a series of catalyst beds contained in one or more reactors. After cooling, the reactor effluent passes into a separator. The gas stream is usually recycled back to the reactor, either directly or after scrubbing to remove hydrogen sulphide, ammonia, and hydrocarbons. The hydrocracking process is highly exothermic, and control of the temperature is necessary by cooling between beds, for example, by recycle hydrogen injection.

The liquid stream from the separator goes to an atmospheric fractionator where light products are removed as gasoline, jet fuel, and one or more middle distillate cuts. The lube oil bottoms fraction is then usually fed to a vacuum

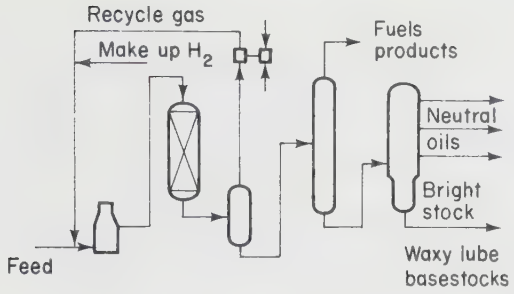


FIG. 41. Simplified process flow diagram for lube hydrocracking. (Courtesy of Imperial Oil, Canada).

tower to be fractionated into streams which, on dewaxing, yield the desired lube products.

Various modifications of this basic scheme are described later.

Catalysts

Catalysts must combine high hydrogenation activity with the desirable selective hydrocracking and hydro-isomerization functions. In addition they must have good activity at relatively low temperatures.

The lube hydrocracking literature reveals that sulphides of nickel and tungsten, nickel and molybdenum and, to a lesser extent, cobalt and molybdenum, can be used to provide hydrogenation activity. Hydrocracking activity is introduced by using a moderately acidic support such as silica-alumina, or magnesia-alumina. Treatment of the support with fluoride or other halides has been claimed to increase the selectivity for viscosity index improvement.[30,31]

Process considerations

Viscosity and viscosity index are two of the major basestock qualities concerning refiners. As described in the following sections, hydrocracking provides greater flexibility than solvent extraction, both in the viscosity and the viscosity index of the feedstock that can be processed and in the quality of the oils that can be produced.

Effect of Process Severity

Higher process severities will usually increase product viscosity index: the structural changes involved also decrease the viscosity. At the same time, higher severities increase the breakdown of lube molecules to low boiling fragments and result in lower lube yields. Figure 42 illustrates these effects.

Variation of Viscosity Index with Boiling Point

Because of molecular scission reactions, hydrocracking gives a lube product boiling from the lower limit of usable oil, about 650°F, up through the boiling

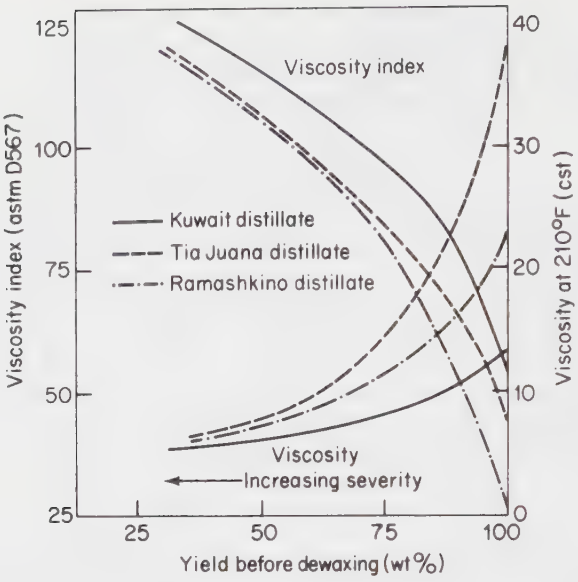


FIG. 42. Effect of hydrocracking severity on viscosity index, viscosity, and yield of 715°F+ lube fractions. (Courtesy of Imperial Oil, Canada.)

range of the feed. A complete viscosity range of lube material is therefore produced from a single de-asphalted residue. The distribution of viscosity index throughout the complete product boiling range depends on both the nature of the feed and the hydrocracking conditions. It is a factor of paramount importance to the refiner who has to control his process to make a specific lube slate.

At low hydrocracking severity, three types of viscosity index distribution have been reported,[1] depending on whether the feed is paraffinic, naphthenic, or aromatic in character, as illustrated in Fig. 43.

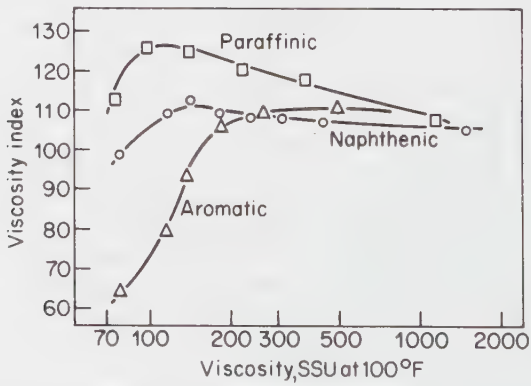


FIG. 43. Effect of feed composition on viscosity index-viscosity distribution. (Courtesy of Imperial Oil, Canada.)

By-Products

In addition to lubricating oils, lube hydrocracking also makes lower boiling products, such as gaseous hydrocarbons, naphtha, and middle distillates, while wax is recovered from the lube fractions themselves. Table XLVII shows typical product distributions for moderate and high severity hydrocracking operations. Jet fuel and middle distillate rather than naphtha are the major light products, as is typical for catalysts of the type used in the process. At low severity, wax yields are about the same as for the feed, but at higher severity some conversion of wax does occur.

TABLE XLVII

Product Distributions in Lube Hydrocracking. (Courtesy of Imperial Oil, Canada)

Crude source	Texas			Middle East		
Viscosity index (VIE) of dewaxed base oil	105–95*			130		
Product distribution	*Wt%*	*Vol%*		*Wt%*	*Vol%*	
H_2S–NH_3	1.7			2.6		
C_1–C_4	1.7			2.6		
C_5–180°F	1.1	1.6		2.6	3.7	
180–350°F	3.8	4.5		6.5	8.1	
350–550°F	14.2	15.6		22.7	25.8	
550–650°F	10.7	11.3		16.9	18.6	
650°F+	68.4	73.4		48.0	53.3	
(Dewaxed oil)			(58.8)			(42.2)
(Oil-free wax)			(14.6)			(11.1)
Total	101.6	106.4		101.8	109.5	

* Slate comprising light and heavy neutrals and Bright Stock.

The fuels by-products are low in sulphur. Hydrocarbon composition depends on feedstock quality, but typical feeds produce jet fuel fractions with low aromatic contents and high smoke points. Gasoline fractions are predominantly naphthenic in character and make excellent reformer feed.

Oxidation Stability of Industrial Oils

Resistance to oxidation as measured in various laboratory tests is mainly important for industrial oil basestocks. This property has two aspects: the inherent oxidation stability of the oil and its response to inhibitors.

The elimination of sulphur and nitrogen compounds, some of which act as natural inhibitors, can cause hydrocracked oils to be more sensitive to oxidation than conventionally refined oils.

There is ample evidence that hydrocracked bases have exceptional inhibitor response and give formulated products of excellent oxidation stability. Several groups of workers[1,4,15,19] have demonstrated that the ASTM oxidation life of turbine oils based on hydrocracked products is two to three times longer than that of similar oils made from solvent-refined basestocks.

Engine Test Results

Engine deposits, rust and wear are low for motor oils based on hydrocracked bases, and are equivalent to conventional products in both single-and multi-grade formulations. No ring sticking problems have been found. Additives used in these tests were reportedly conventional types and were not specifically designed for oils made by hydrocracking.

Because of excellent inhibitor response, their performance is equivalent and in some instances superior to that of conventional products.

Engine test data indicate that hydrocracked oils make satisfactory engine oil basestocks. Products incorporating these basestocks have no serious quality disadvantages relative to conventional products, but some modification of additive systems may be necessary to improve high-temperature stability. Another factor requiring design of new additives is additive compatibility, which is reported to be a problem with certain gear oil additives and polyacrylate viscosity index improvers.[33] Hydrocracked basestocks offer advantages over conventional solvent oils in oxidation stability and bearing corrosion stability, and in the performance of multi-grade oils through reductions in viscosity index improver content.

Gulf HDS Process[19]

This process is a severe hydrodesulphurization process applied to residua with the intent of distilling from the product lube distillates which are acceptable in yield and quality without further processing. Typical yields and qualities are given in Tables XLVIII, IL and L and Figs 18, 44, 45 and 46. The process is described in the section on the hydrodesulphurization of residua.

Esso low-cost integrated lubricant plants[20,21,22]

Owing to rapidly rising construction costs it is important to minimize the investment in new plants, since capital charges are an important component of

TABLE XLVIII

Comparison of Yields of Lube Oil Charge Stocks for Kuwait HDS Atmospheric Bottoms and Virgin Kuwait Atmospheric Bottoms. (Courtesy of Gulf Research, Pittsburgh)

Lube oil charge stock	Viscosity SUS at 210°F	Yield: Vol % of crude		
		Virgin Kuwait	Kuwait HDS products	
			Type II HDS*	Type III HDS†
Light distillate	40	10.0	16.3	15.5
Medium distillate	61	8.0	4.7	7.0
Heavy distillate	108	5.0	8.3	7.0
De-asphalted oil	195	7.3	5.2	5.7
Total		30.3	34.5	35.2

* 650°F+ product contained 1.0% sulphur.
† 650°F+ product contained 0.62% sulphur.

TABLE IL

Properties of Lube Distillates from 0.8 per cent Sulphur HDS Atmospheric Tower Bottoms. (Courtesy of Gulf Research, Pittsburgh)

	Light distillate	Medium distillate	Heavy distillate
Inspections			
Gravity, API	28.2	25.1	21.8
Viscosity, SUS: 100°F	100.9	—	—
150°F	—	104.7	310
210°F	39.1	52.8	96.4
Pour point, °F	+70	+100	+120
Sulphur, wt. %	0.35	0.43	0.57
Nitrogen, wt. %	0.07	0.10	0.13
Carbon residue, Rams, wt %	0.08	0.10	0.74
ASTM distillation % at °F			
10%	710	803	927
59	738	857	972
90	805	915	1040
Dewaxed oil			
Yield. vol. % waxy dist.	70.8	70.3	87.1
Gravity, API	26.7	23.7	20.3
Viscosity, SUS: 100°F	122	441	2138
210°F	37.0	56.0	111.2
Viscosity Index	58	68	62
Pour point, °F	0	−5	0

TABLE L

Gulfinishing of HDS Dewaxed Raffinates. (Courtesy of Gulf Research, Pittsburgh)

	Light distillate		Medium distillate		Heavy distillate	
	Feed	Product	Feed	Product	Feed	Product
Yield, vol %		98.9		99.9		99.7
Hydrogen consumption: scf/bbl		22		17		34
Product inspections						
Gravity, °API	32.4	32.8	28.5	29.3	27.0	28.1
Viscosity, SUS: 100°F	96.2	97.1	289	294	830	728
210°F	39.0	39.1	51.4	51.5	79.2	75.3
Viscosity Index	96	97	95	94	93	96
Colour, D1500	L4.0	L0.5	L5.5	L1.0	>8.0	L3.5
Pour point, °F	0	+5	0	+10	0	+5
Sulphur, wt %	0.04	0.03	0.12	0.06	—	—
Haze Point: 48 hr						
Intensity of haze		Bright		Bright		Bright
Characteristic of haze		No haze		No haze		No haze

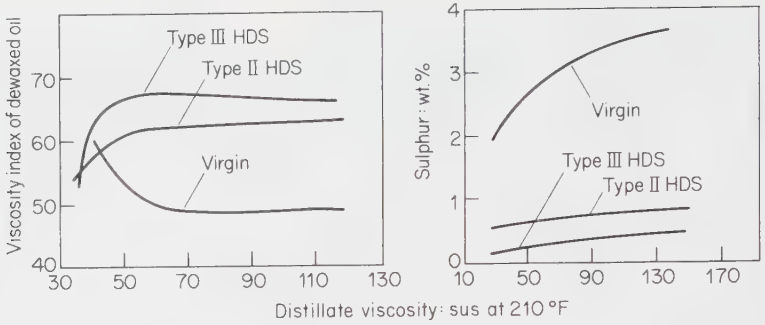


Fig. 44. Quality of HDS distillates. (Courtesy of Gulf Research, Pittsburgh).

the cost of finished lubricating oil base stocks. This is difficult to do if the new plants are basically copies of units built in the past. J. D. Bushnell of Esso Research has described an approach that has proved successful in meeting this challenge—an integrated lubricant plant design.

Four basic processing steps are incorporated in this type of plant. Propane de-asphalting removes asphalt from vacuum pipestill bottoms to permit manufacture of high-viscosity oils; phenol extraction removes unstable low viscosity index materials; hydrofining improves colour; and propane dewaxing reduces the pour point to as low as $-18°C$. None of these processes is new; what is new is the improvement and simplification brought about by process optimization, engineering developments, and integration.

An example of integration is the combining of two basic steps, phenol extraction and hydrofining, into one process unit, called a 'Phenolfiner', as shown in Fig. 47. Waxy distillates from a vacuum pipestill are processed through the phenolfiner and propane dewaxing units. Severe extraction produces motor oils and turbine oils of 95 to 115 viscosity index. Mild extraction produces high yields of pale oils of excellent colour and colour stability, suitable for use as industrial lubricants, even from crudes of high nitrogen content.

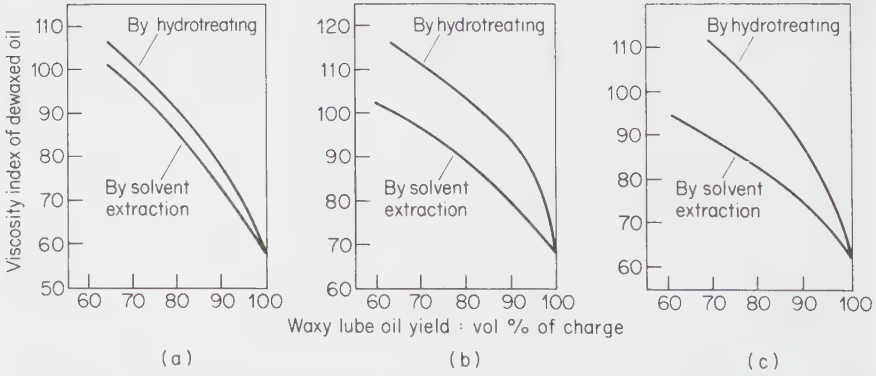


Fig. 45. (a) HDS light distillate, (b) HDS medium distillate, (c) HDS heavy distillate. (Courtesy of Gulf Research, Pittsburgh.)

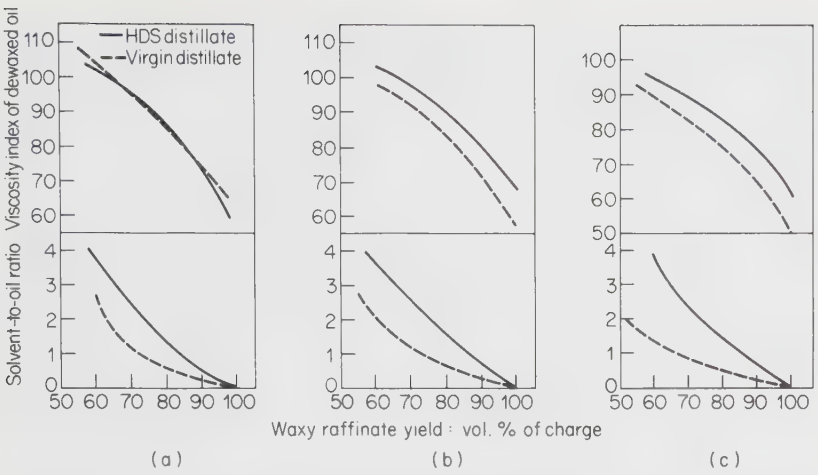


FIG. 46. (a) Furfural extraction of HDS light distillate, (b) Furfural extraction of HDS medium distillate, (c) Furfural extraction of HDS heavy distillate. (Courtesy of Gulf Research, Pittsburgh.)

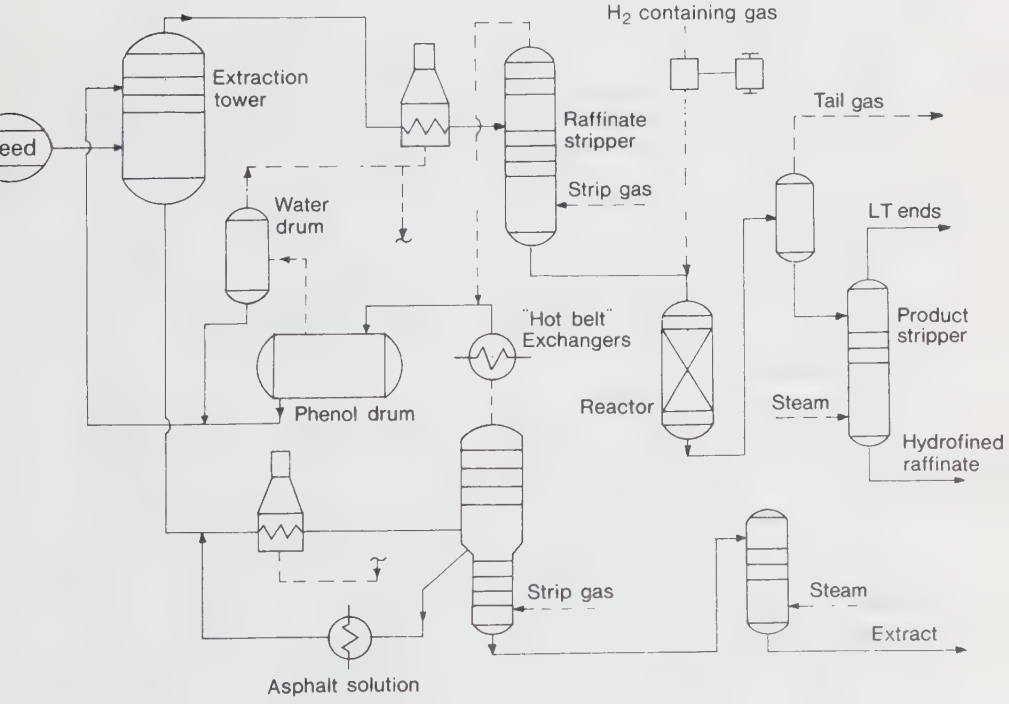


FIG. 47. The Phenolfiner unit. (Courtesy of Exxon Research, NJ.)

Vacuum pipestill residuum processed through the propane de-asphalting unit yields de-asphalted oils of 150 to 225 SSU/210° F. If processed through the phenolfiner and dewaxing units, a bright stock of 90–100 VI is produced. If processed only through the dewaxer, a cylinder stock is obtained which can be used for gear lubrication or other uses requiring high viscosity, but not high VI or good colour.

Naphthenic lubricants may be made by running the naphthenic distillate through the phenolfiner at high yield, and by-passing the dewaxer. Feed is charged to the lower part of the extraction tower and phenol of the desired water content sent to the top. Raffinate and extract solutions pass through furnaces into their respective single-tower solvent recovery sections. Final traces of phenol are removed in the lower parts of these towers by means of stripping gas. The overhead vapour from the strippers passes through exchangers where the bulk of the phenol is condensed at a higher temperature than is normally available from refinery steam. The heat of condensation is used to vaporize propane in the de-asphalting and dewaxing units. This arrangement is a key feature of the integrated plant, and its success depends on the excellent thermal stability of phenol. High heat-transfer coefficients and large temperature differentials in these exchangers permit maximum recovery of heat with minimum surface. To provide even more heat to the asphalt solution in the de-asphalting unit (where foaming can be a problem) this stream can be heat exchanged with hot liquid taken from the extract stripper flash zone and recycled back to the extract furnace inlet. In this manner, virtually the total heating duty of the entire plant is provided by the furnaces in the phenolfiner.

Extract product is steam stripped in the explosivity corrector. Stripped raffinate is hot enough for hydrofining and is mixed with the hydrogen-rich gas before passing through the reactor. Tail gas is removed in a high-pressure separator. Hydrofined raffinate is steam stripped for light ends removal and sent to tankage. The flow of the propane de-asphalter is conventional, but a multi-stage contacting tower is used, and all heat needed for solvent recovery is provided by the phenolfiner.

Thus the solvent system of the phenolfiner replaces the steam boiler needed in a non-integrated de-asphalting unit. This arrangement recovers more heat than could conveniently be recovered internally in the phenolfiner, and thus part of the de-asphalting heat load is free. The operating costs of the plant are accordingly reduced.

The dewaxing unit uses the same propane solvent as the de-asphalter. Solvent handling facilities are integrated with those of de-asphalting, so that a common compressor, condenser, solvent drum, and spare solvent pump can be used. The auto-refrigeration capability of the solvent eliminates the need for a separate refrigeration system. Scraped surface exchangers, which require a large plot area, are not required. The high filter rates normally obtained permit using only two filters for plants having a finished oil capacity in the range of 2000 to 4000 bd. Dewaxing response is particularly outstanding on bright stock, and a haze-free product can be made with low dilution ratios.

A simplified flow scheme of the propane dewaxing plant is shown in Fig. 48 and illustrates how the de-asphalter solvent system is integrated. Hot feed containing a trace of dewaxing aid is mixed with liquid propane, cooled by

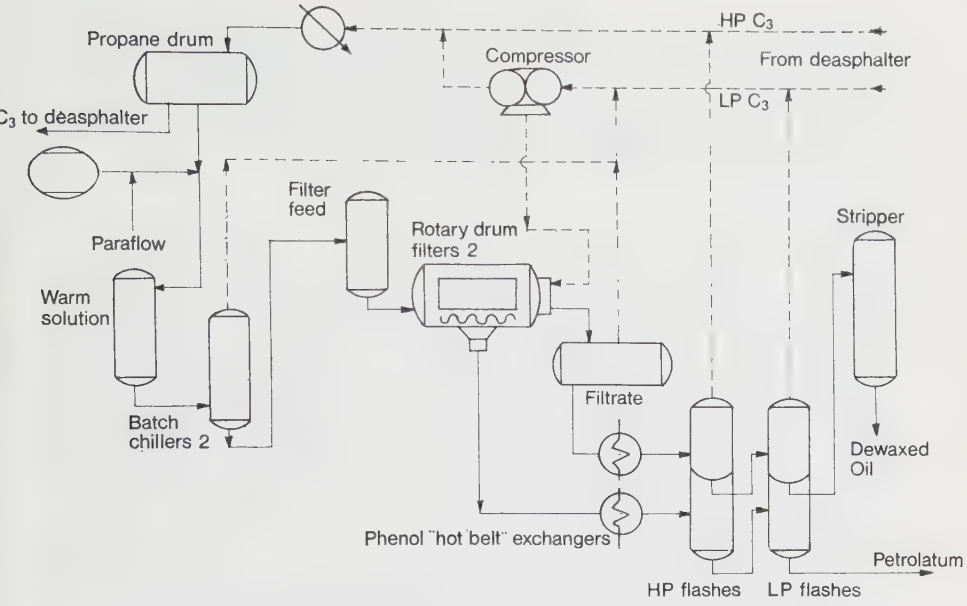


FIG. 48. Propane dewaxing unit. (Courtesy of Exxon Research, NJ.)

exchange and sent to a warm solution surge drum. From here it is pressured into one of two batch chillers where the solution is cooled to the desired filtration temperature by auto-refrigeration. Some of the propane solvent vapour from the filters goes to the suction of the compressor. While cooking takes place in one chiller, the cold slurry in the other chiller is routed to the filter feed drum and the chiller is refilled with warm solution. The batch chillers are operated by an automatic sequence controller.

Wax is removed from the filtrate in two enclosed rotary drum filters. Interstage propane gas from the compressor is used as blow gas to dislodge the cake from the filter drum, and to supply the filtering pressure differential. Filtrate and wax slurry from the filters are heated by condensing phenol in the exchangers and passed to high-pressure flash drums where most of the solvent is removed and returned to the propane condenser. The remaining solvent is removed in low-pressure flash drums and goes to the compressor suction, while the dewaxed oil is flash corrected and dried in a vacuum stripper.

High- and low-pressure propane vapours from the de-asphalter join the similar streams from the dewaxer. Compressor discharge vapour is condensed, and the liquid propane from both the de-asphalter and the dewaxer enters a common surge drum, from which the streams are re-pumped to the respective processes. Thus all of the refrigeration and other compression duty for both dewaxer and de-asphalter can be handled by a single centrifugal compressor, thereby minimizing investment and maintenance. Choice of drive for this machine must, of course, reflect the local situation; if a gas turbine with a waste-heat boiler is used, the steam generated therein will normally exceed the total on-site steam requirement (for heating, stripping, vacuum jet ejectors and steam tracing) for the entire plant.

The integrated plant needs only two compressors, instead of five for separate units. Furnaces are reduced from four to two. Filters are reduced from five to two for the same size plant. The number of pumps drops from 39 to 24, heat exchangers from 44 to 32, and towers and drums from 49 to 37. As a result, the space required for the plant was reduced by 20 per cent. Investment and processing costs are reduced proportionately.

Refining of Waxes[25]

The subject of the dewaxing operation is the removal of wax from an otherwise desirable lubricating-oil fraction, and there is a good market for the extracted wax (slack wax) if it can be efficiently de-oiled. This may be accomplished either thermally by a 'sweating' process, which is really a fractional melting operation, or by solvent de-oiling. In the 'sweating' process, the molten slack wax, containing some 10 to 20 per cent of oil, is run on to a series of trays and allowed to solidify. These trays have a false bottom of gauze below which is a layer of water, and are mounted on trolleys. After solidification of the wax the trolleys are passed through a long 'sweating' tunnel, heated to the temperature required to melt the paraffins of lower melting point, which then drain away, carrying most of the oil with them. The process is continued until the melting point of the residual material has been raised to the desired temperature. The final runnings, which are low in oil content but high in wax content, may be recycled, or else re-sweated on their own; thus good yields are obtained and waxes of varying melting points can be manufactured.

While crystalline waxes of a predominantly normal paraffinic character may be satisfactorily prepared from distillate wax stocks by 'sweating', this is not true of the higher melting point micro-crystalline waxes, consisting mainly of iso- and cyclo-paraffins, since these do not form well-defined crystals that readily occlude oil. Micro-crystalline waxes must be prepared by solvent de-oiling of short residues. Solvent de-oiling may also be used to manufacture crystalline waxes from distillate stocks. The solvents and types of equipment used are as applied for conventional dewaxing. The slack wax feed is melted and dissolved in hot solvent. The mixture is chilled, filtered, and washed. The recovered wax is re-pulped with solvent, filtered again, washed, and transferred to a solvent recovery system. The temperature of filtration is adjusted to produce wax of the desired melting point. High quality micro-crystalline waxes are manufactured from short residue slack wax feedstocks by separating out the very high melting waxes of a brittle nature.

The traditional finishing treatment for crystalline waxes is either contacting with sulphuric acid, followed by treatment with activated clay and lime, or alternatively percolation at a moderate temperature through activated clay or bauxite. In acid treatment disposal of the spent acid, clay and lime represents an additional expense. With the percolation process appreciable quantities of solids require handling, including frequent regenerations of bauxite by roasting.

BP Wax Hydrofinishing Process

The above treatments are now being superseded by hydrotreating, as in the case of lubricating oils. Figure 49 shows the BP wax hydrofinishing process. The

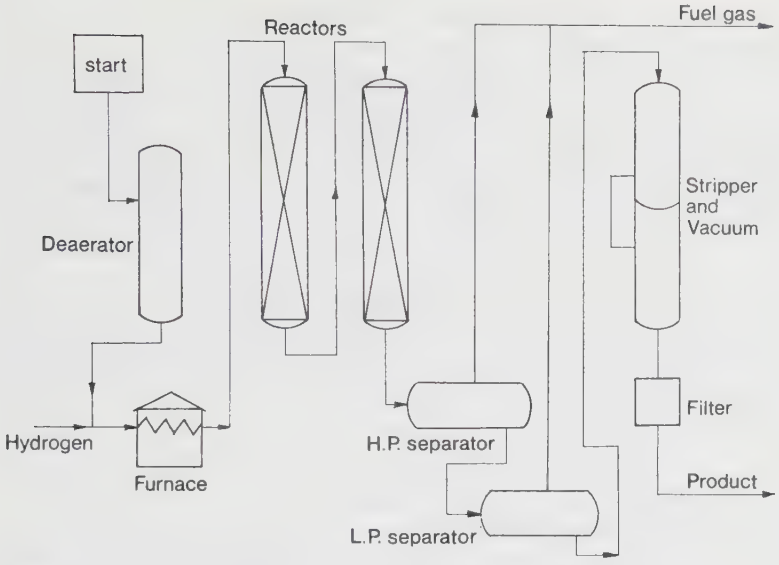


FIG. 49. BP wax hydrofinishing process. (Courtesy of BP Research, London.)

liquid feedstock is mixed with a hydrogen-rich gas, heated to the treatment temperature and passed downflow through two reactors in series containing two entirely different catalysts. After two-stage gas separation and adjustment of the wax temperature the treated wax is steam-stripped, and dried under vacuum. The wax is finally filtered to remove any fine adventitious material.

The process operates under moderate conditions of temperature and pressure. High-purity hydrogen is not essential, and gas from catalytic reformers is a suitable source of hydrogen-rich gas. Consumption of hydrogen is very small, as might be expected from the general chemical composition of crystalline petroleum waxes, and because of the modest gas flow requirement, once-through gas flow should normally be possible in refineries having catalytic reformers.

The process is essentially a mild hydrotreatment in which trace compounds that are responsible for light and heat instability are eliminated, and hence a product yield in excess of 90 per cent can be achieved. The high yield, compared with acid treatment or bauxite treatment, and the simplicity of plant operation are the outstanding attractive features of wax hydrofinishing.

Esso DILCHILL Wax Hydrofining[25]

This process allows integration between dewaxing and refined wax manufacture, eliminating the need for a costly, separate recrystallization plant. In combination with either lube or wax hydrofining, this represents a total process package for dewaxing, wax manufacture, and lube and wax finishing.

The slack wax obtained from a conventional plant is of little or no value as a speciality wax because it contains too much oil, too much low-melting-point

soft wax, and too many colour bodies. Further expensive processing is required to upgrade it to a commercial product such as refined wax.

The process is illustrated in Fig. 36—described earlier. Slack wax cake from the filters is mixed with warm solvent to dilute the remaining oil and to bring the mixture to a temperature required to dissolve only the undesired low-melting wax. The resulting wax-solvent mixture is then refiltered at higher temperature to produce high-melting hard wax, meeting the required specification oil content of commercial refined waxes. The quality of the refined wax is essentially equal to that obtained from a conventional solvent recrystallization plant.

The wax product obtained is virtually identical with that produced by redissolving conventional slack wax and recrystallizing it. The critical properties of melting point, penetration, oil content, blocking temperature, and normal paraffin content are all similar.

TABLE LI
Hydrofining Waxes. (Courtesy of Esso Research)

Crude source	San Joaquin		San Joaquin		Panhandle		Panhandle	
	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Colour	13 TR*	−12 Say.	+0 Say.	+30 Say.	12 TR*	+1 Say.	18 TR*	+30 Say.
U.S.P. Acid, % reduction		30		80		35		80
Sulphur, % reduction		50				35		

* Tag Robinson.

Since the crystals are compact, very little oil is occluded within the crystalline mass itself. Furthermore, since the proper melting point product can be made simply by mixing with warm solvent, the soft wax which is to be redissolved must be deposited only on the outside of the more or less spherical crystals. The softer wax is crystallized near the crystallizer outlet and deposited conceptually in the form of layers on the nucleus of hard wax in the centre.

Three unusual characteristics of the crystals make them uniquely suitable for carrying out the warm-up de-oiling operation without an intermediate recrystallization operation. First, the crystals are initially so large that they still filter well after the soft wax is redissolved. Secondly, the compact, coherent structure does not allow the crystals to fall into pieces when mixed with warm solvent. Thirdly, the 'layered' structure allows the undesirable soft wax to be redissolved without affecting the core of the crystal.

The refined wax is fed to a wax HYDROFINER. The HYDROFINER enables the de-oiled wax to meet colour, odour, and FDA purity requirements for sale as refined wax. In this manner, one integrated unit can produce dewaxed oil and completely refined wax, using in-step operation. Some typical feed and quality data are given in Table LI.

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III REFINING OF RESIDUA AND HEAVY CRUDES

Perhaps the most important development in refining technology in the past decade has been the successful extension of hydrodesulphurization with hydrocracking to upgrade residua and heavy crudes to lighter and more marketable products. This change has been forced upon the refining industry by two factors, the need to reduce atmospheric pollution from burning high-sulphur fuels, and the energy demand and competitive pressure to increase the yield of usable products from the crude, with declining markets for residual fuel oils.

Air pollution abatement problems[1] and legislation have called for a reduction in the emission of sulphur dioxide in flue gases. Contributing in part to the total sulphur dioxide emission is the sulphur present in residual fuel oils. Present petroleum sources account for approximately forty per cent of the total sulphur dioxide emitted to the atmosphere in the Free World. Hydrotreating processes are available for removing sulphur from fuel oils prior to burning for supplying heat and electrical energy.

Residua and heavy crude desulphurization is now a commercially[2,3,4,5] proven technology capable of upgrading most heavy crudes attractively and economically. The process upgrades the whole crude, rejects none, produces no unsaleable product, and produces a pipe-line quality crude refinable in existing refineries with no intermediate pretreating or special handling. Also important are the environmental considerations of a non-contaminating plant and clean products. There is a high probability of a reasonable return on investment, and the capability of conservation of energy via total conversion of heavy crude to usable liquid petroleum.

The cost for these operations will depend to a very large extent on the sulphur schedules and specifications on fuel oils which will be established by legislative bodies in various parts of the world. The business factors, economics, and fuel oil demand will determine what process or process combinations should be selected for producing the fuel oils.[6,7,8,9]

Most major oil companies have made significant contributions to this field. There is, however, a general similarity in the processes and the main concepts. The pilot plant successes have been confirmed by major commercial plant operations in Esso, Union Oil, and Gulf refineries. By 1972 the processes were firmly established, and they achieve over 97 per cent desulphurization of high-sulphur residual oils.

The Esso/Union GO-FINER is described elsewhere in this chapter, and to provide a typical picture of the fundamentals of the hydrodesulphurization of residua, the Esso/Union RESIDIFINER and the Gulf HDS processes will be described here.

The merits of hydrotreating processing alternatives are considered for supplying low-sulphur fuel oils. The processes are: (1) Vacuum Gas Oil Desulphurization, (2) De-asphalted Oil Desulphurization, and (3) Direct Residuum Desulphurization (including heavy crudes, tar sands). Product quality data and blended fuel oil inspections are presented. The choice of what process to employ for removing sulphur from fuel oils is governed primarily by (1) sulphur level and the volume of the market, (2) crude source from which the fuel is obtained, and (3) manufacturing costs.

TABLE LII

Typical Poor Qualities of Residua and Crudes

	Accepted fuel	Vac. G.O. distillate	Commercial residual fuel	Light Arabian residua	Heavy Arabian crude	Heavy Venezuelan crude	Heavy Canadian crude
Quality							
API gravity	>20	20	13.9	18.5	28.2	8.5	15.7
Sulphur, wt%	<0.5	3.06	3.3	2.93	3.4	4.0	3.6
V, ppm	<20		38	14	86	440	203
Nitrogen, ppm	<10		10	7	24	89	
Asphaltenes, wt %	<0.5						
Con. carb., wt %	<5		9.7		13.2	13.8	13.8
Naphtha insol., wt %	<0.5	0.55			9.5		

The need for the hydrodesulphurization of residua and heavy crudes is reflected in the quality data given for such stocks in the untreated state and after hydrodesulphurization, in Tables LII and LIII. A list of the limitations and the need to overcome these is given in Table LIV.

There are two main concepts: firstly the disruption by hydrogenation of molecules containing polar elements such as oxygen, nitrogen, sulphur and metals, to give hydrocarbons, and secondly, the improvement in the catalytic activity and life to levels comparable with those achieved with the hydrodesulphurization of middle distillates, and with a desulphurization of over 90 per cent.

The technology has been described by Arey and Mayer of Esso Research, and the following review of the basic facts is taken freely from pertinent publications of Esso, Union, and Gulf.

It should be noted that the severe hydrodesulphurization and the hydrogenation of residua and heavy crudes are described in the present chapter with respect to the product qualities which are necessary to satisfy the fuel oil market. The aspects of these processes concerned with the volume change, cracking feedstocks, etc. are dealt with in Chapter 14.

TABLE LIII

Typical Good Qualities of Hydrotreated Residua and Crudes

	Accepted fuel	Vac. G.O. distillate	Commercial residual fuel	Light Arabian residua	Heavy Arabian crude	Heavy Venezuelan crude	Heavy Canadian crude
Quality							
API Gravity	>20	25.5	20.6	25.1		22.7	
Sulphur, wt %	<0.5	0.4	0.36	0.12	0.19	0.08	
V, ppm	<20		14	0.3	6	19	
Nitrogen, ppm	<10		5	0.5	2	8	
Asphalt, wt %	<0.5	Nil					
Con. carb., wt %	5	0.8	4.3		2.9	2.8	
Naphtha insol., wt %	<0.5	Nil					
Process data							
% Desulphurization			81.93				
Scf/B. H_2 consumption			720				
Conversion							
1 050°F+			24 50				
200°F+			10-25				

TABLE LIV

CRITICAL FACTORS
1. *Limitations of Unrefined Residual Fuels Causing Low Sales*
Viscosity
Sulphur
Metals
Asphaltenes
Conradson carbon
Poly-nuclear aromatics
Nitrogen content
Atmospheric emissions
Naphtha insolubles
2. *Problems in Processing to Upgrade Quality*
De-activation of catalyst by:
Complex polar contaminants
Complex metals complexes
Complex asphaltenes
High costs
3. *Pressing Needs*
Improved catalyst activity and life
High sulphur removal
Hydrogenation to lighten products
Low hydrogen consumption
Optimization of feed treatment
Low costs
Higher quality products

The processes for hydrodesulphurization of fuel oils have been described earlier, and only those processes primarily concerned with the hydrodesulphurization of heavy distillates, residua, and heavy crudes are described here.

Vacuum Gas Oil Hydrodesulphurization[10]

Under the proper processing conditions and with suitable catalysts, vacuum gas oils can be processed to give very low sulphur content fuel oils. Typical product inspections obtained for several desulphurization operations are given in Table LV. A block diagram of the vacuum gas oil process showing how it can be used to produce several grades of low-sulphur fuel oil is shown in Fig. 50. This process is capable of producing a 0.2–0.3 wt per cent sulphur product for use directly as fuel oil or as a blend stock for producing heavy fuel oils containing 1–2 wt per cent sulphur.

De-asphalted Oil Hydrodesulphurization[11]

Large quantities of fuel oil containing less than 1 per cent sulphur generally cannot be made using only the vacuum gas oil process. An extension of the vacuum gas oil operation can be achieved by adding a de-asphalted oil hydrodesulphurization unit. A block diagram showing this extension is shown

TABLE LV

Typical VGO HDS Product Inspections. (Courtesy of Exxon Research, NJ)

Crude source	Safaniya	Tia Juana	Tia Juana
Gravity, °API	24.5	24.0	28.4
Sulphur, wt %	0.4	0.24	0.18
MNI, wt %	0	0.05	0
Conradson carbon, wt %	0.08	0.23	0.06
Viscosity, universal secs.			
at 100°F	230	782	83
at 130°F	120	242	57
Pour point, °F	80	85	55
ASTM D-1160			
IBP, °F	450	498	471
10%, °F	710	786	544
50%, °F	860	877	693
80%, °F	913	955	847
FBP, °F	969	990	955

in Fig. 51. In this operation vacuum residuum is de-asphalted to produce de-asphalted oil and an asphalt product. These additional operations permit a much deeper cut into the barrel of crude, and asphalt yields as low as 10 per cent crude are possible. The sulphur can be removed from the de-asphalted oil to produce a very low sulphur content product. This material can be marketed as a very high quality low-sulphur fuel oil or can be used as a blend stock for asphalt and other heavy residual fuels to make greater quantities of low-sulphur fuel oil. An inspection of a typical de-asphalted oil product is compared with its corresponding feed in Table LVI.

Direct Residuum Hydrodesulphurization[12,13,14,15]

The direct residuum process offers means for producing greater quantities of low-sulphur fuel oil. In this operation the entire reduced crude fraction is

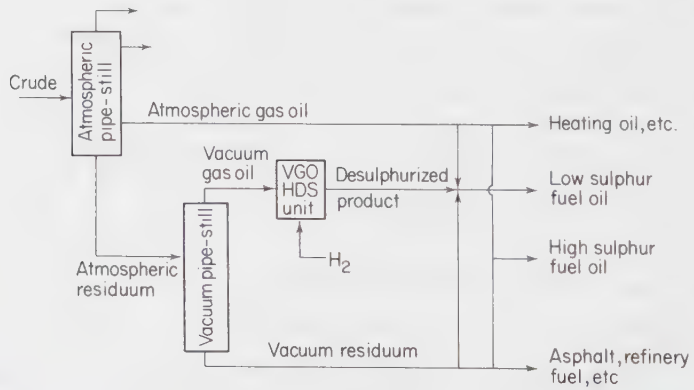


FIG. 50. Vacuum gas oil hydrodesulphurization process for low sulphur fuel oil.

TABLE LVI

Solvent De-asphalting/Hydrotreating. (Courtesy of Exxon Research, NJ)

Process	De-asphalting of 1000°F+ Vacuum residuum from Middle East crude	RESIDFINING of De-asphalted oil
Product	De-asphalted oil	Feed to catalytic cracking
IBP cut point (°F)	1000+	650+
Yield on vacuum residuum (vol. %)	77.9	76.3
Gravity (°API)	14.0	19.5
Sulphur (wt %)	2.88	0.43
Nitrogen (wt %)	0.31	0.195
Conradson carbon residue (wt %)	8.2	2.6
Metals (wppm)		
Nickel	7.3	0.07
Vanadium	18.3	<0.01
Hydrogen/Carbon weight ratio	0.133	0.140
Aniline point (°F)	—	224
Refractive index at 67°C	—	1.502
Chemical H_2 consumption (scf/B)		525

processed, and the low-sulphur product can be marketed as a low-sulphur fuel oil. In this operation the need for a vacuum pipe-still, a de-asphalter, and other equipment required for the previous processes can be eliminated. A simplified schematic diagram for this process is shown in Fig. 52. Of the processes discussed so far, the direct residuum process requires less equipment and involves the least number of steps to produce a low-sulphur fuel oil. However, it should be pointed out that the processing conditions are more severe in this case, since the reduced crudes contain more metals and other residues than the corresponding vacuum gas oils and de-asphalted oils. The catalyst used for the process must be tolerant to metals, and heavy asphaltic and carbon residue.

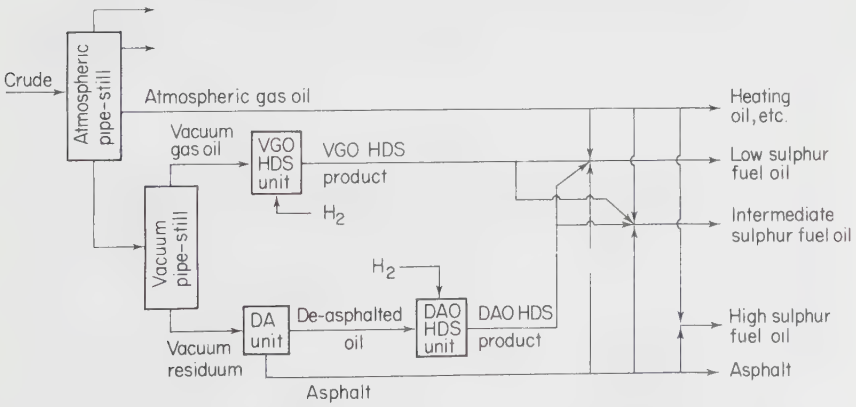


FIG. 51. Vacuum gas oil and de-asphalted oil hydrodesulphurization for low sulphur fuel oil.

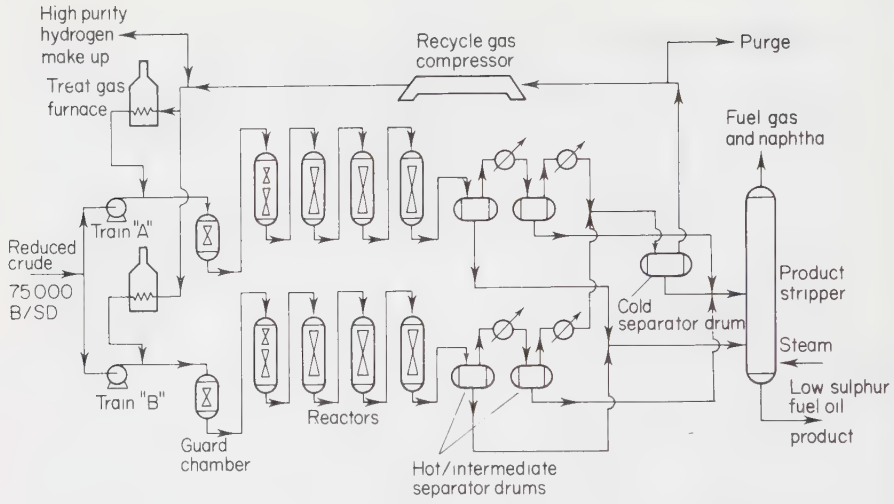


FIG. 52. RESIDFINING unit configuration. (Courtesy of Exxon Research, NJ.)

Data on light and heavy atmospheric and vacuum residua for Arabian, Jobo, Venezuelan, and Canadian crudes are given in Tables LVII to LX inclusive.

Typical investment and utility costs for the process are given in Table LXI.

Desulphurization Catalysts[16,17,18]

Many catalytic formulations are known to have activity for sulphur removal from residual fuel oils. Generally these catalysts are made from Group V, VI, or VIII elements impregnated on various kinds of catalyst supports. Commercial desulphurization catalysts of this type are on the market today and many are suitable for vacuum gas oil and some de-asphalted oils. However, on residual stocks, and on some de-asphalted stocks containing a higher proportion of metals and asphaltic residue, these catalysts are not satisfactory, since rapid deactivation may occur. A comparison of a conventional desulphurization catalyst and an improved catalyst on a heavy Middle East residuum stock in a

TABLE LVII

Feed and Product Qualities from Hydrotreating JOBO Crude. (Courtesy of Exxon Research, NJ)

	Feed	Product
Gravity, °API	8.5	22.7
Sulphur, wt %	4.0	0.08
Nickel, ppm	89	5
Vanadium, ppm	440	19
Conradson carbon residue, wt %	13.8	2.8

TABLE LVIII

Contaminant Removal from Conventional Atmospheric Residuum. (Arabian Heavy Atmospheric Residuum.) (Courtesy of Exxon Research, NJ)

	Feed	Product
Sulphur, wt %	3.4	0.19
Nickel, ppm	24	2
Vanadium, ppm	86	6
Conradson carbon residue, wt %	13.2	2.9

TABLE LIX

Heavy Arabian Vacuum Residuum* New Catalyst, 93 per cent HDS High Conversion Operation

	Product qualities			
	S (Wt %)	N (Wt %)	Metals V/Ni (wppm)	CCR (Wt %)
Liquid product fraction				
C_5/430°F	0.004	0.010	—	—
430/650°F	0.044	0.061	—	—
650/1 050°F	0.240	0.150	0.1/0.4	0.45
1 050°F+	0.820	0.270	25/18	12.6
Feedstock fraction				
650/1 050°F	2.94	0.087	0.04/0.19	0.9
1 050°F+	6.0	0.480	205/64	27.7

* Values represent start-of-run conditions.

TABLE LX

RESIDFINING Process with RT-621 Catalyst for Vacuum Residua and Heavy Crudes. (Courtesy of Exxon Research, NJ)

	Vacuum residuum (Arabian Heavy)	Heavy crude	
		Venezuelan	Canadian
Feed			
Gravity, °API	2.6	8.8	11.1
Sulphur, wt %	5.3	4.0	4.3
Conradson carbon residue, wt %	25.9	15.5	12.0
Nickel, wppm	45	117	63
Vanadium, wppm	176	432	183
Contaminant removal			
HDS, %	82	97	94
1 050°F+ conversion, %	40	64	35
Conradson carbon removal, %	57	78	68
Nickel removal, %	60	95	92
Vanadium removal, %	78	97	94

TABLE LXI
Typical RESIDFINING Investments and Utilities

Crude	Arabian Light	
Cut range	650°F+	1 050°F+
Unit capacity, kB/SD	71.1	25.6
Investment costs, k$ (1st Q. 1978 US Gulf Coast)		
Direct material	44 000	32 200
Direct labour	3 800	2 400
Total M and L	47 800	34 600
Catalyst costs		
Initial charge, k$	5 700	4 430
Make-up cost, ¢/B	26	55
Utilities requirements		
Fuel fired, kBTU/b	34	34
Electrical power, kWH/b	1.3	2.6
Steam produced, lb/b		
125 psig	32	41
600 psig	13	12
Cooling water, gal/b	53	58
Boiler feed water, gal/b	8	6
Process water, gal/b	2	2

pilot plant test is shown in Fig. 53. An inspection of this Figure leaves no doubt about the better performance of the new type catalyst. These results show a drastic improvement in activity maintenance. New improved catalysts offer the best possibilities for reduced hydrodesulphurization costs.

Exxon has developed a tailor-made family of proprietary (RT) catalysts for atmospheric residua hydrotreating processes. This catalyst has a uniform small pore structure which reduces the accessibility of the highest molecular weight heterocyclic molecules to the active sites within the catalyst pores. These hydrogen-deficient high molecular weight materials tend to form coke and

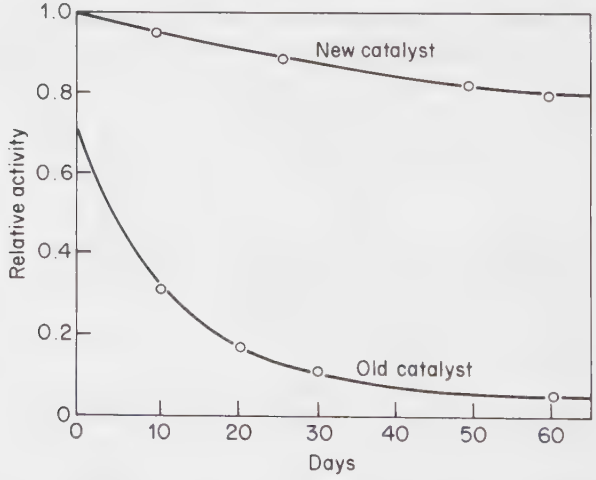


FIG. 53. Comparison of relative activity for old and new catalyst. (Courtesy of Exxon Research, NJ.)

TABLE LXII

Contaminants are Concentrated in Asphaltenes. (Courtesy of Exxon Research, NJ)

	Jobo crude			Cold Lake crude		
	950°F − fraction	950°F + fraction		950°F − fraction	950°F + fraction	
		Non-asphaltenes	Asphaltenes		Non-asphaltenes	Asphaltenes
Amount,						
Wt % on feed	43.9	39.0	17.1	40.4	40.2	19.4
Composition						
Sulphur, wt %	3.1	4.01	5.59	2.81	4.72	7.56
Nickel, ppm	0.5	40	441	2	25	328
Vanadium, ppm	0	160	2 309	0	50	823
Conradson carbon residue, wt %	0.1	14.0	48.8	0.1	9.3	42.0
Nitrogen, wt %	0.15	0.73	1.85	0.09	0.48	1.19

deposit metals such as vanadium and nickel at the active sites. Consequently, catalyst life is extended substantially by 'screening' out the high molecular weight molecules from the catalyst.

As shown in Table LXII the largest asphaltene molecules contain high concentrations of the contaminants. The preparation of the catalyst base is critical, specifically with regard to the average pore size and the uniformity of pores, as shown in Fig. 54. In addition, careful attention would be needed to determine the amount of catalytically active metals required and how they should be added to the base to ensure maximum activity.

Pore Structure. The catalyst with the uniform pores has a significantly higher initial activity than the catalyst with non-uniform pores. This is reflected by the plot of relative temperature required to meet a fixed product sulphur specification as a function of time, which is also shown in Fig. 54. The reason for this lower activity for the catalyst with non-uniform pores is thought to be related to the 'screening' phenomenon observed with catalyst RT-2. At the severe conditions required for deep contaminant removal, some of the large asphaltene molecules deposit coke and metals on the catalyst interior. In the case of the non-uniform catalyst these deposits are sufficient to block large areas of the interior when deposited in the narrow 'necks' of the pores. In contrast, the uniform pore catalyst has a minimum number of these narrow openings and the contaminants can therefore deposit more uniformly.

A more complete treatment of pore size effects is presented in a recent paper by Spry and Sawyer.[17] Referring to Table LXIII, for the range of pore sizes studied sulphur, Conradson carbon residue, and nitrogen removal rates are not significantly diffusion-limited, whereas metal removal is. These types of studies were used to select the preferred average pore size for the catalyst system.

Metals Addition. In addition to pore structure, the amount of catalytic metals added and the method by which they are added were also found to be critical

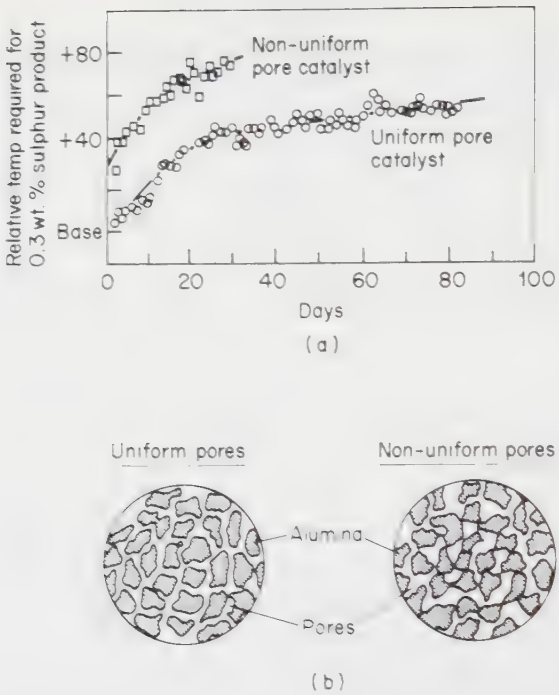


FIG. 54. (a) Uniform pores critical to performance of RT-621 (Arabian heavy atmospheric residuum). (b) Schematic of enlarged catalyst cross-section. (Courtesy of Exxon Research, NJ.

factors in producing an active catalyst for this service. In Table LXIV and Fig. 55 the results of three experimental metals impregnation techniques are illustrated. Technique I was used to prepare a catalyst having a large loading of catalytic metals. Technique II was used to prepare a catalyst of slightly lower metals loading. Technique III was used to prepare two samples, one being comparable to the high loading of the first sample and the other having a considerably lower loading. Following calcination, all samples were analysed

TABLE LXIII

Influence of Average Pore Size on Contaminant Removal. (Courtesy of Exxon Research, NJ)

	Catalyst		
	A	B	C
Relative pore size	100 (Base)	73	118
Relative removal rate			
Sulphur	100	112	89
Conradson carbon residue	100	112	89
Nitrogen	100	112	89
Metals	100	63	113

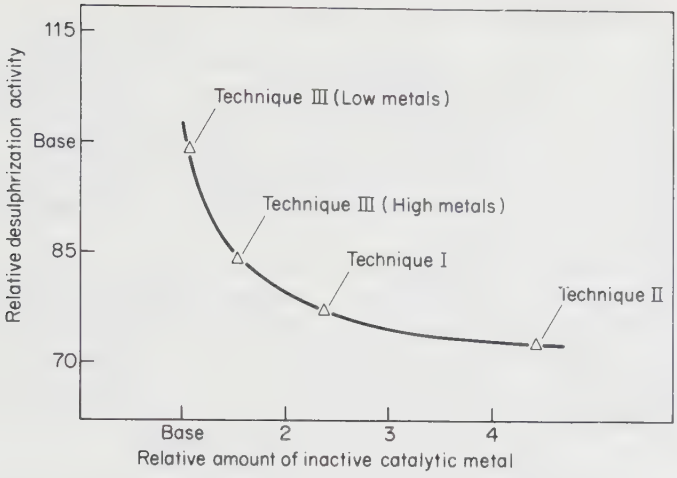


FIG. 55. Metals impregnation technique critical to catalyst activity. (Courtesy of Exxon Research, NJ.)

to determine the amount of inactive agglomerated metals present. The catalysts prepared by Technique III were considerably better than those prepared by the other techniques. In fact, the sample with the lowest total metals loading appeared to be the best in terms of catalytic metals utilization.

Metals Chemistry. This has been examined by NMR and ESR surveys of vanadium on spent catalyst materials. The NMR and ESR spectroscopic studies made of the vanadium in crude oil and deposited during hydrodesulphurization on alumina-supported cobalt-molybdenum catalysts discharged from commercial GO-FINING and test reactors show that at low loadings (to 0.7%) the vanadyl species ($VO(2+)$) dominates, and that it is in a different form from that in crude oils or on calcined supports in the presence of sulphur; that at higher loadings, to approximately 10 per cent, vanadium is present mainly as a diamagnetic species, possibly a sulphide or oxysulphide, and that the maximum loading of this species is probably a mono-layer; at higher loadings, the balance of the vanadium forms V(sub 2) S(sub 3) crystallites.

TABLE LXIV
Impregnation Technique Affects Metals Utilization. (Courtesy of Exxon Research, NJ)

	Technique		
	I	II	III
Metals level	High	Intermediate	High
Relative amount of inactive (agglomerated) metals	2.5	4.3	1.4

Quality of Fuel Oils

In addition to the sulphur content of residual fuels, the viscosity and pour points of these materials are of interest. The amount of viscosity reduction is largely a function of the amount of desulphurization obtained. As the amount of desulphurization is increased, the viscosity of the residual fuel is reduced, The same trend is also observed in the pour points of the products. Figures 56 and 57 summarize the trends obtained with typical stocks as a function of desulphurisation for this stock.

A very interesting result was observed when blending a 50/50 mixture of vacuum gas oil desulphurized product and de-asphalted oil desulphurized product with asphalt. When making blends of these two materials the pour point of the blended fuel oil was less than the pour points of either the feed or the desulphurized blend stock. Thus it appears that the asphalt is an effective pour point depressant. The reduction in pour point obtained for blending various amounts of asphalt and blend stock is shown in Fig. 58.

Hydrogen Consumption

One of the major costs in desulphurization is the hydrogen consumption arising during the desulphurization operation. Hydrogen consumption increases as greater percentages of sulphur are removed from the residual fuel oil and also as heavier fractions are processed. The explanation for this is that as sulphur is removed from the heavier fuel oil components higher molecular weight

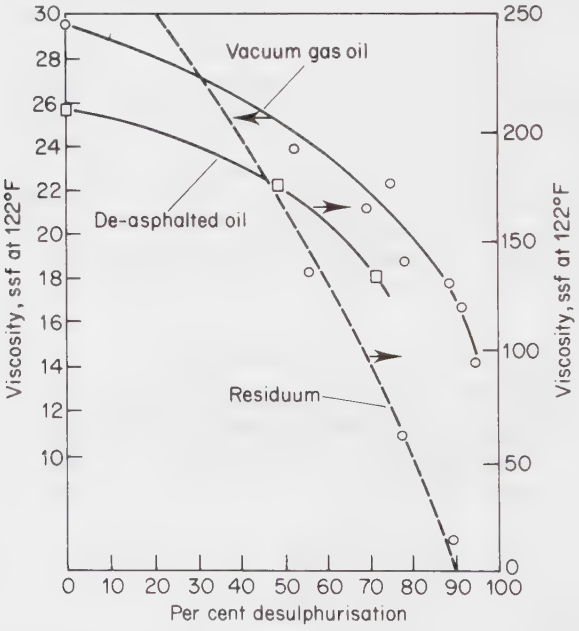


Fig. 56. Viscosity reduction versus desulphurization. (Courtesy of Exxon Research, NJ.)

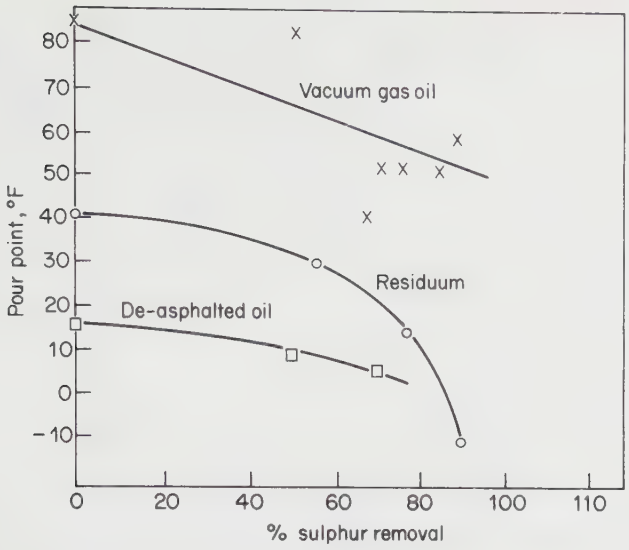


FIG. 57. Typical pour point reduction versus desulphurization. (Courtesy of Exxon Research, NJ.)

condensed ring aromatic compounds containing sulphur are involved. In order to remove the sulphur from the heavier boiling components considerable saturation of aromatic rings is necessary and some cracking occurs. For this reason the hydrogen consumption at the same per cent desulphurization is greater for total reduced crudes than their companion vacuum gas oils and de-asphalted oils. A plot showing the hydrogen consumption versus per cent desulphurization is presented in Fig. 59.

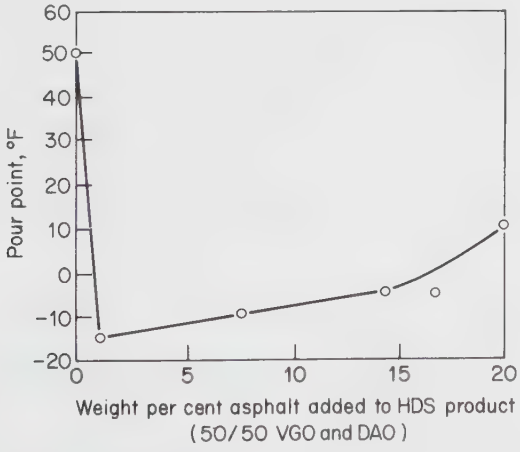


FIG. 58. Pour point depression with the addition of asphalt. (Courtesy of Exxon Research, NJ.)

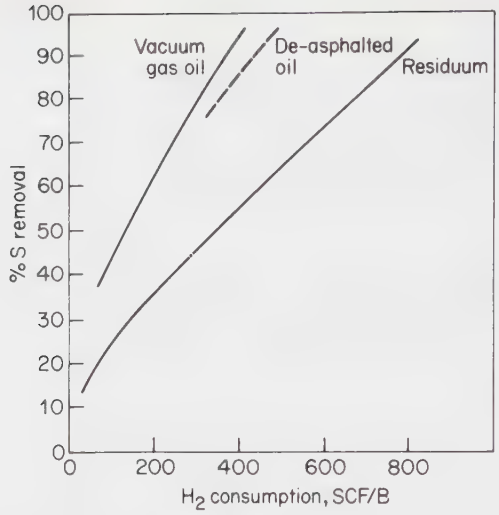


FIG. 59. Typical hydrogen consumptions. (Courtesy of Exxon Research, NJ.)

Cost of Desulphurization

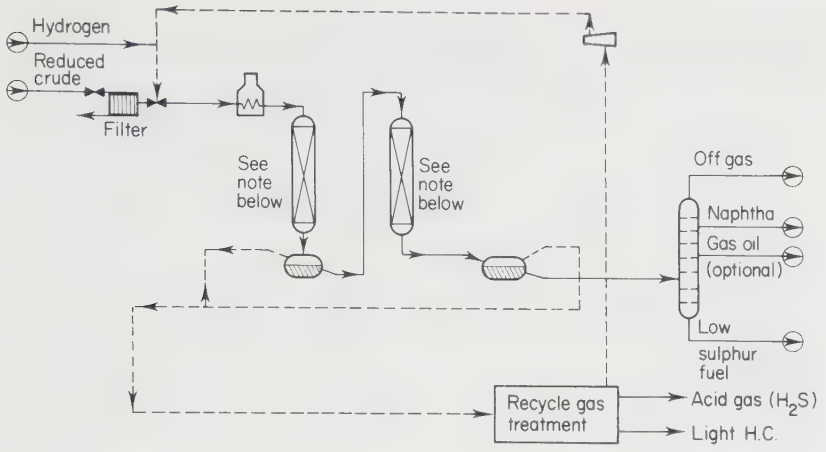
It is extremely difficult to prepare a generalized overall investment and operating cost for the desulphurization of fuel oils. The reason for this is the variable nature of the important items affecting the cost. These are: (1) Crude source and desired sulphur level of the product, (2) location of the facility, and (3) the raw materials costs, principally hydrogen. It is true, that quite accurate investment and operating costs can be estimated for on-site equipment at a specific location. However, the total cost associated with the production of low-sulphur fuels must also include the cost of off-site facilities, and at times these costs can be nearly equal to the on-site costs. For the above reasons the costs can be somewhat misleading unless all the details are known. Therefore a detailed cost breakdown will not be attempted here.

A major contributor to the desulphurization operating cost is the cost of hydrogen. The hydrogen cost is affected principally by the value of the fuel used to produce the hydrogen. Generally the cheapest available fuel source is used, and this can vary from natural gas to heavy fuels. Another factor affecting the cost of producing low-sulphur fuel oils is the depth of desulphurization desired, and in general the cost increases as larger amounts of sulphur are removed from the fuel oil barrel.

Gulf HDS Process[19,20,21]

This process has been developed for very heavy crudes such as the oils recovered from tar sands. The status of world-wide heavy crude production and upgrading is summarized as follows:

1. Oil sands yield a heavy, sour bitumen of little use except as road-surfacing material.



Note: Number of reactors and reaction trains is variable

FIG. 60. Gulf HDS—types III and IV. (Courtesy of Gulf Research, Pittsburgh.)

2. Upgrading involves coking and hydrodesulphurization, produces a synthetic crude refinable by current technology, and petroleum coke that is unsaleable because of high sulphur content.
3. Upgrading operations consume a major part of the capital investment in oil-sands projects, and are the prime area for the application of chemical processing technology.

The Gulf HDS Process has been designed to upgrade heavy crudes having the above characteristics. The process is a fixed-bed catalytic hydrogenation process, which is operated at moderately elevated temperatures and pressures for periods of 6–12 months. The general configuration of the process and flow therein are illustrated in Fig. 60. The primary reactions are desulphurization, demetallization, denitrogenation, and upgrading of asphaltenes. The last is related to contaminant removal, since contaminants (S, N and metals) are bound to a large extent in asphaltene molecules and their removal causes fragmentation of the asphaltenes. This fragmentation, followed by hydrogen saturation, produces marked upgrading of API gravity, viscosity, and carbon residue. As a run progresses, however, the contaminants laid down on the catalyst (coke, metals) cause catalyst deactivation, which must be compensated for by increases in reaction temperature. When the temperature reaches a predetermined level, or the deposits reach a limiting level, the run is terminated, and the catalyst is replaced. The catalyst is remarkably active and long-lived in the face of deposits which have been known to reach 65 per cent of the original catalyst weight. Catalyst reactivation is not possible via conventional regeneration, since metals are not removed and catalyst pores remain metals-filled.

Typical data using the Gulf process for the hydrodesulphurization of heavy crudes are given in Table LXV. Most of the data on this process concern catalytic cracking feedstocks and products, which are discussed in Chapter 14.

TABLE LXV

Properties of Heavy and HDS Upgraded Heavy Crudes. (Courtesy of Gulf Research)

	Orinoco (Morichal)		Canadian (Lloydminster)	
	Untreated	HDS upgraded estimated	Untreated	HDS upgraded*
Properties				
API Gravity	9.6	23.6	15.7	29.1–26.3
Viscosity, SUV at 210°F	2650	60	—	—
Sulphur: %	4.13	0.28	3.6	0.22–0.77
Metals: Ppm (Ni + V)	468	27	203	3.0–30
Assay (vol. %)				
Naphtha (C_5–375°F)	<1	7.5	6	11–12
Mid-distillate (375–650°F)	11	32	23	37–40
Vacuum gas oil (650–1050°F)	39	43	37	39 33
Vacuum residue (1050°F+)	49	23	34	15–16

* Range of yields and product inspection over length of pilot plant run.

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Every attempt has been made to recognize this help by the references and bibliography included, and apologies are hereby offered to any fortuitous omission.

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B.P.	London	B.N.O.C.	London
Shell	The Hague	Imperial	Sarnia

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